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The structure and photocatalytic studies of N-doped TiO_2 films prepared by radio frequency reactive magnetron sputtering

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Abstract

N-doped TiO_2 films were prepared by a radio frequency reactive magnetron sputtering (RF-MS) deposition method from an undoped TiO_2 target in a mixture of Ar/N_2 atmosphere on heated quartz glass substrates. The structures and properties of the N-doped were studied by XRD, Raman, XPS, TEM, ultraviolet (UV)–vis and PL spectroscopy. By analyzing the structures and photocatalytic activities of undoped and N-doped TiO_2 films under ultraviolet and visible light irradiation, the probable photocatalytic mechanism of N-doped TiO_2 films was investigated. Because many oxygen defects are caused in films by nitrogen doping, it is presumed that nitrogen doping and oxygen defect induced the formation of new states closed to the valence band and conduction band, respectively. The cooperation of nitrogen and oxygen defects leads to a significant narrowing of the band gap and greatly improves the absorption in the visible light region. It is found that the degradation efficiencies of N-doped TiO_2 films greatly decreased under ultraviolet irradiation, but slowly improved under visible light irradiation, compared with the undoped TiO_2 film. It is suggested that the N-doped TiO_2 films are formed for the nitrogen to occupy oxygen defect sites directly. The doped nitrogen ions and oxygen defects act as recombination centers that reduce the lifetime of photo-induced electrons and holes, thereby resulting in the decrease of photocatalytic activity under ultraviolet light illumination.

Keywords: N-doped TiO_2 films; Photocatalysis; Oxygen defects; Methyl orange

1. Introduction

TiO_2 is the most widely used photocatalyst for the decomposition of various organic pollutants because of its inexpensiveness and nontoxicity. Moreover, the photocatalysis based on TiO_2 is found to have several advantages over conventional oxidation processes, such as complete mineralization of the pollutants, use of the near- ultraviolet (UV) or solar light, no addition of other chemicals, operation at room temperature, and so on [1,2]. Although it has been widely investigated in the past decade, some problems still remain in its practical applications [3–7]. The band gap energy of TiO_2 (3.0–3.2 eV) requires UV light irradiation, and thus only a small portion of the solar spectrum is absorbed in the UV region [8]. Hence, much effort has been devoted to preparing a TiO_2-based photocatalyst that is capable of efficient utilization of the visible light constituting the main part of the solar spectrum. Up to now, many strategies, including the doping of TiO_2 with transition metals, the synthesis of reduced forms with TiO_{2-x} structure by plasma treatment, and the doping of TiO_2 with anionic nonmetals have been investigated.

Even though the modified TiO_2 by doping with transition metals can be prepared successfully, only a few can indeed improve the photocatalytic activity [9–11]. However, most of them reduce the photoactivity because of their role as recombination centers [12,13]. Furthermore, many transition metals are toxic and can diffuse from TiO_2 to the environment during the application, which may lead to a second pollution and limit its further studies. In

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comparison with metals, the TiO_2-doped with nonmetals have drawn great attention due to their nontoxic feature. Many attempts have been made in the direction of N, C, or S anion-doped TiO_2 photocatalysis because it has good potential for the utilization of solar energy [14–18]. The most feasible and successful approach among these anions seems to be N-doping, but the mechanism for exhibiting visible light activity in this system is still controversial. For example, Asahi et al. [19] claimed that the doped N atoms narrow the band gap of TiO_2 by the mixing of N2p and O2p states; thus, making it capable of absorbing visible light and demonstrating the activity for the decomposition of acetone and methylene blue in wavelengths up to 550 nm. Irie et al. [20] argued that the isolated narrow band located above the valence band is responsible for the visible light response. In addition, Ihara et al. [21] insisted that it is oxygen vacancies caused by N-doping that contribute to the visible light activity. Generally, the N concentration doped in TiO_2 is below 2 at% for most of the N-doped TiO_2 cases. Clemens Burda enhanced the doped N up to 8 at% by employing the direct amination of nano-titania particles, which are catalytically active and can absorb well into the visible region up to 600 nm [22]. The C-doped TiO_2 is also a studying hotspot that could show obvious visible light activity besides the N-doped TiO_2. For example, Khan et al. [23] reported that carbon doping of TiO_2 could extend the photoactive region for water oxidation from 400 to 535 nm, thus leading to a large increase in the water splitting efficiency under white-light illumination.

Until now, many studies have been focused on N-doped TiO_2 powders by doping N atoms into oxygen sites of TiO_2 using calcinations in N_2 or NH_3 atmosphere [20], wet chemical processes [21], and spray pyrolysis [24], but so far, few reports have been found for the photocatalysis of N-doped TiO_2 films prepared by magnetron sputtering. Although the TiO_2 films received less attention due to the poor photoactivity, they have a good potential for the applications in self-cleaning [25,26], anti-fogging, and anti-bacterial glasses [27,28], thus needing further investigation.

Magnetron sputtering is the most widely used method for thin film preparation [29–31] and is often used to construct uniform, well crystallized, and large-area composite films. The film thickness, composition, and structure can be easily controlled by adjusting the sputtering power, substrate temperature, partial pressures of sputtering and reactive atmosphere, sputtering time, and distance from the target to the substrate [32]. By introducing N_2 into a vacuum chamber as a reactive atmosphere, the N-doped TiO_2 films can be prepared. It is also found that the sputtering power and substrate temperature are two important parameters that affect the structure and composition of the N-doped TiO_2 films.

This article presents results of a systematic investigation of N-doped TiO_2 films reactively sputtered on heated quartz glass substrates. More than at 2% nitrogen atoms were doped in the TiO_2 films, which can extend the visible light absorption up to 600 nm. It reports on the effects of N doping on film crystallinity, absorption in the range of UV and visible light, optical band gap, photoluminescence property, and photocatalytic activity under UV and visible light irradiation.

2. Experimental

2.1. Film preparation

The N-doped TiO_2 films were prepared using the radio frequency reactive magnetron sputtering (RF-MS) method operating at a frequency of 13.56 MHz in a commercial system JPD-1501. The stainless steel chamber was evacuated down to a base pressure of 2.0×10^{-3} Pa with a turbomolecular pump backed up with a mechanical pump. The high-purity argon and nitrogen were employed as sputtering and reactive gasses, respectively, and the working pressure was 1.0 and 0.4 Pa. An undoped sintered TiO_2 ($\varnothing$ 56×5, 99.9%) was used as the sputtering target. The substrate was placed parallel to the sputtering target surface with a substrate target distance of 100 mm. For comparison, the undoped TiO_2 film was prepared in a mixture of high-purity argon and oxygen, and the working pressure was 1.0 and 0.6 Pa. The substrate temperature was monitored by a thermocouple fixed on the backside of the substrate holder and kept at 300 °C during sputtering. The flow rates were controlled with a mass flow meter and the pressures were measured with an ion gauge. Prior to the sputter-deposition step of the films, a movable shutter was interposed between the target and the substrates. In addition, the target was pre-sputtered in an undoped argon atmosphere for 5–10 min to clean the target surface. Three N-doped films were prepared by changing the sputtering powers. They were named as NTiO-1 (75 W), NTiO-2 (95 W), and NTiO-3 (130 W). The sputtering time was 90 and 60 min for the N-doped TiO_2 films and the undoped TiO_2 film, respectively.

2.2. Characterization

The X-ray diffraction (XRD) pattern obtained on a Panalytical X'pert X-ray diffractometer using Cu Kα radiation at a scan rate of $0.05^\circ(2\theta)$/s was used to determine the film structure. The Raman spectra were recorded on a RENISHAW spectrometer equipped with an optical microscope at room temperature. For excitation, the 514.5-nm line from an Ar^+ ion laser was focused with an analyzing spot of about 1 μm on the sample under the microscope. The phase identification and morphology were studied using transmission electron microscopy (TEM) (Jcol Co., 1200EX, Japan). The UV–vis reflection (R) and transmittance (T) spectra of as-prepared films were obtained using a UV–vis spectrophotometer (NKD 7000) from 200 to 800 nm, and the film thickness (d) and absorption coefficient (α) were calculated from the R and T spectra. The band gap energies of as-prepared films were obtained using the extrapolation of the film absorption