



Photocatalytic degradation of dye and NO_x using visible-light-responsive carbon-containing TiO₂

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ABSTRACT

Ultraviolet- and visible-light-responsive titania was synthesized and employed in the photomineralization of NO_x and dyes. A carbon-modified titania photocatalyst was prepared by an impregnation method using anatase TiO₂ particles as the raw material and ethanol as the carbon source. Carbon-containing titanium dioxide with the anatase phase prepared at 200 °C, exhibited high photocatalytic activity for the degradation of gaseous NO_x and decolorization of aqueous methyl orange under visible-light illumination. The calcination temperature in this impregnation process plays an important role in the formation and resultant content of carbonaceous structure on TiO₂ surface and affects both the optical and the photocatalytic properties of TiO₂. The carbonaceous species on the TiO₂ surface, shown by photoluminescence spectroscopy, Raman, UV–vis, infrared spectroscopy, and X-ray photoelectron spectroscopies, plays an important role in the visible-light absorption and photocatalytic degradation rates for NO_x and methyl orange.

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1. Introduction

Since the discovery of the photoelectrochemical splitting of water using titanium dioxide electrodes [1], researchers have extensively studied semiconductor-based photocatalysis. Currently, titanium dioxide is the most commonly used material for photocatalysts owing to its strong redox ability and widespread use in air purification systems, water treatment, deodorization, self-cleaning and sterilization coatings [1–3], and other applications. In environmental applications, TiO₂ exhibits excellent photocatalytic abilities for mineralizing NO_x, SO_x, and VOCs under solar irradiation; TiO₂ absorbs photons and evolves active oxygen species, such as OH radicals and O₂^{•−} ions, through reaction with H₂O and O₂ adsorbed on its surface. The high oxidation potentials of these nascent active oxygen species result in the decomposition of many different pollutants [2,3].

A large number of photocatalytic applications use nano-sized anatase phase TiO₂. A light source of less than 388 nm in wavelength can activate a TiO₂ photocatalyst with an energy gap of 3.2 eV. In the solar light spectrum of the earth's surface, the energy associated with the UV region of wavelength from 280–400 nm accounts for only approximately 4% of the total energy. Meanwhile, the 400–700 nm wavelength visible-light region accounts for 45% of the total energy. Furthermore, UV light intensity, i.e.,

0.1–5 μW/cm², is very low in indoor illumination situations limiting the domestic and indoor commercial applications for TiO₂. As a result, visible-light-responsive photocatalysts receive much more attention for increasing solar and indoor lighting energy utilization. Previous studies considered the sol–gel method, sputtering plasma, metal–organic chemical vapor deposition (CVD), physical vapor deposition (PVD), and metal ion-implantation methods to enhance the visible-light response of TiO₂. However, the equipment required for these methods is expensive, and mass production is difficult. Materials such as CdS, TaN, TaON, and InVO₄ are known to function as visible-light-responsive photocatalysts. However, in developing their widespread, large-scale use for any practical application, the cost and stability of the material must be considered. Few feasibility studies exist for these methods and materials for industrial-scale production owing to their higher cost, environment pollution issues, and material instability. In contrast, an impregnation process followed by low-temperature calcination is a practical way to produce visible-light-responsive TiO₂ materials because it enables the manufacturer to modify the commercial product effectively with only low operating costs.

Herein, we present a facile and cost-effective method for the preparation of high-efficiency visible-light-responsive TiO₂ developed using an impregnation method. The impregnation method is widely used to modify metal oxide particles and films. Normally, the impregnants used for the improvement of visible-light response in materials are noble metal salts, such as Pt, Au, and Ag [4–7]. The anions of N, S, C, P are inexpensive materials for the same purpose [2,3,8], but the processes used for their incorporation into the TiO₂

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lattice as dopants are complicated and include the sol–gel method, sputtering plasma, metal–organic chemical vapor deposition, and ion implantation. Carbon-modified titanina is reported to exhibit good visible-light-responsive activity [4,9–21]. A carbon-modified photocatalyst has a great potential for practical application owing to the low cost of carbon sources. Vapor deposition methods (CVD and PVD) for the preparation of C-TiO₂ are quite effective [18–21], but rendered impracticable by expensive apparatus and complex processes. Therefore, wet-chemical [9–15] and mechanochemical [16] methods have been developed in order to reduce production costs. Visible-light-responsive C-TiO₂ can be synthesized by modified sol–gel processes using tetrabutyl orthotitanate as the precursor under controlled calcination conditions [9–15]. Kish et al. developed a commercial process for a carbon-modified photocatalyst prepared by the hydrolysis of titanium tetrachloride with tetrabutylammonium hydroxide [13–15]. However, these organic and inorganic precursors and related methods are also expensive and complicated, respectively. Thus, the most practicable approach for the mass production of visible-light-responsive TiO₂ is to directly modify the commercial UV-responsive TiO₂ material by a simple process. Herein we report the development of a simple impregnation process to prepare our carbon-containing photocatalyst using ethanol as the carbon source. The activities of the synthesized photocatalysts were evaluated for the oxidation of NO_x and decolorization of dye under illumination by visible light. The characteristics of these synthesized photocatalysts were also investigated for a satisfactory explanation of the visible-light activity.

2. Experimental

2.1. Experimental conditions and characterization

The carbon-containing, nano-structured TiO₂ samples were produced by the impregnation method. TiO₂ powder (10 g, Ishihara ST01) was added to anhydrous ethanol (100 mL) in a 250 mL flask. The solution was uniformly agitated at 500 rpm for 1 h, and then, the precipitated TiO₂ was obtained after drying at 70 °C on a hotplate. The dried powder was calcinated in air under controlled temperatures (100–300 °C) for 5 h. Sample nomenclature is defined as follows: TiO₂-X is the photocatalyst prepared by the impregnation process with calcination at X °C (100, 200, 250, and 300 °C) for 5 h.

The photocatalyst crystal phase was identified using X-ray diffraction with Cu K α radiation (Rigaku D/Max RC). Material compositions and the content of carbonaceous species were determined by X-ray photoelectron spectroscopy (Perkin Elmer SSI-M probe XPS system). A diffuse-reflectance scanning spectrophotometer (Shimadzu, UV-2450) was employed to obtain the UV–vis absorption spectra of the powders. The reflectance data were converted to the absorbance values, $F(R)$, based on the Kubelka–Munk theory. Photoluminescence spectroscopy (PL) was carried out using a luminescence spectrometer (Jasco FP-6500LE), under excitation with 325 nm irradiation. The functional groups on the TiO₂ surface were observed with an infrared spectrometer (Thermo Nicolet Magna 750 II) equipped with a diffuse-reflectance device. Photocatalyst surface structures were identified by a Raman spectrometer (Renishaw 1000B), and a scattering experiment was conducted with a low-power green laser (30 mW) at 532 nm for 10 s.

2.2. Photocatalytic capacity of photocatalyst

2.2.1. Gaseous compound: degradation of NO

In this work, a continuous flow system is used for the degradation of NO_x over TiO₂ [4,9,10,19]. A cylindrical Pyrex glass vessel

($\phi \times H$, 10 cm \times 4 cm) was used as the photoreactor for the degradation of NO_x, and a sample dish was located inside the vessel containing the TiO₂ powder. LEDs (visible light) or a black lamp (UV light) provided a light source with an intensity of 1 mW/cm². Two types of LED devices (blue and green) and one black lamp were used to provide visible light and UV light, respectively. The main LED and UV peaks are observed at 465, 515, and 352 nm, respectively. NO_x degradation was carried out at room temperature using an air stream containing 1.0 ppm NO as feedstock. Two mass flow controllers (MFCs) (Brooks 5850E) manipulated the relative humidity (RH=50%) in the feeding stream. The reaction gas in the feeding stream passed through the vessel containing TiO₂ powder (0.2 g) at a flow rate of 1 L min⁻¹, with a residence time of 0.31 min. An on-line chemiluminescent NO_x analyzer (Eco Physics, CLD 700 AL) continuously monitored NO and NO₂ concentrations for gas analysis in the outlet.

2.2.2. Aquatic compound: decolorization of dye

Methyl orange (C₁₄H₁₄N₃NaO₃S) was used to investigate the photocatalytic activity of the TiO₂ samples under UV and visible-light illumination. 0.2 g of the photocatalyst was dispersed in methyl orange aqueous solution (10 ppm) by means of ultrasonic waves for 20 min. The suspension was then stirred, and samples were drawn at intervals. The reaction temperature of 27 °C was maintained by a water bath. After stirring at 300 rpm for 30 min in the dark, the adsorption equilibrium was reached, and then, the UV-A or visible light source with an intensity of 1.7 mW/cm² was applied and samples were drawn at intervals for analysis of the concentration of methyl orange. A UV–vis spectrometer (Metertech SP-880) was used to determine the concentration of methyl orange by the absorbance of the solution at a wavelength of 465 nm. No detectable degradation of the dyes was observed in the absence of the catalyst or from irradiation with UV and visible light alone. The photocatalytic decolorization reaction followed a pseudo-first order rate law, which was consistent with previous literature [10,22]. The reaction rate law can be expressed as $\ln(1 - X) = -kt$, where k and X are the reaction rate constant and the conversion of methyl orange, respectively.

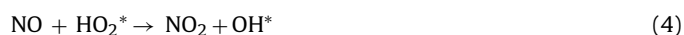
3. Results and discussion

3.1. Photocatalyst activity under UV and visible-light irradiation

Many researchers use NO oxidation to determine the photocatalytic reactivity in various TiO₂ photocatalytic applications [4,9,19,22,23]. The electron–hole pair ($e^- - h^+$) generated upon light excitation is trapped at the TiO₂ surface as spatially separated redox active sites. Some studies report the formation of reactive oxygen species, such as superoxide ion (O₂^{•-}), atomic oxygen (O), O⁻, OH and HO₂ radicals on the surface of TiO₂ irradiated with UV light [2–4]. The general mechanism of NO_x oxidation by a photocatalyst is given below. Hydrogen ions and hydroxide ions are dissociated from water. The active oxygen species are produced on the TiO₂ surface.



Nitric monoxide is oxidized to nitric acid or nitrous acid by active oxygen species. Based on the gas-phase chemistry of NO_x [24], NO is converted to HNO₃ as a consecutive photooxidation via a NO₂ intermediate. Nitric acid is then formed on the catalyst surface.



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