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Efficient visible-light induced photocatalysis on nanoporous nitrogen-doped titanium dioxide catalysts

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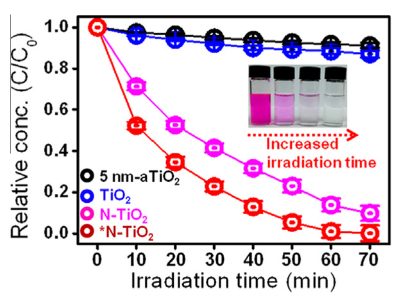
HIGHLIGHTS

- The nanoporous N-TiO_2 photocatalysts were successfully synthesized at room-temperature.
- The *N-TiO_2 was irradiated with visible-light to improve the surface hydroxylation of the N-TiO_2 surface.
- The N- and *N-TiO_2 exhibited excellent photocatalytic and antibacterial activities.
- Moreover, the *N-TiO_2 exhibits excellent photocatalytic stability.

GRAPHICAL ABSTRACT



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ABSTRACT

To use visible-light more efficiently in photocatalytic reactions, nanoporous nitrogen-doped titanium dioxide (N-TiO_2) was synthesized at room temperature, without thermal treatment, using modified sol–gel processing and ultrasound irradiation. In addition, the N-TiO_2 was irradiated with visible-light to improve the hydrophilicity of its surface. The calculated surface energy of visible-light irradiated N-TiO_2 (*N-TiO_2) was 69.1% higher than the value of 91.47 mJ m^{-2} obtained for N-TiO_2. Under visible-light irradiation, the photocatalytic activity for *N-TiO_2 ($[k] = 4.258\ h^{-1}$) was 22.8 times higher than that for N-TiO_2 ($[k] = 1.871\ h^{-1}$). The *N-TiO_2 photocatalyst was highly recyclable, with a decolorization rate at 92.9% of the initial value after 15 cycles. Interestingly, the *N-TiO_2 photocatalysts showed very strong antimicrobial properties against both Gram-negative *Escherichia coli* (*E. coli*) and gram-positive *Staphylococcus aureus* (*S. aureus*), compared to the results for 5 nm anatase TiO_2 and TiO_2 photocatalysts after visible-light exposure for 3 h. More than ~90.2% of *E. coli* were killed, even after ten cycles of use for the *N-TiO_2 photocatalyst. There were large increases in the photocatalytic and antibacterial activities of *N-TiO_2 relative to those of N-TiO_2; these were the result of the improved surface hydrophilicity of N-TiO_2 by visible-light irradiation. The results presented here contribute significantly toward the development of delicate composite photocatalysts for photocatalytic water/air purification and bactericidal agents.

1. Introduction

Recently, there has been considerable interest in the use of advanced oxidation processes (AOPs) involving the hydroxyl radical, a very powerful chemical oxidant that can quickly remove (or sterilize) a broad range of organic pollutants and bacteria [1,2]. AOPs include semiconductor photocatalysis systems, which are

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attractive for the elimination of harmful aqueous contaminants as a result of their photocatalytic activities, which result from an electronic structure characterized by a filled valence band and an empty conduction band [2]. Among the various semiconductors (TiO_2, WO_3, $SrTiO_3$, Fe_2O_3, ZnO, CdS, and ZnS), TiO_2 is one of the most promising photocatalysts for photoelectric conversion, energy storage, bactericidal effects, photocatalytic treatment of water/air pollutants, and so forth [3]. However, the relatively large band-gap for TiO_2 (3.2 eV for anatase and 3.0 eV for rutile) results in preferential ultraviolet (UV) absorption, and solar energy contains only about 3–4% UV light (λ < 380 nm) [4–6]. The relatively high rate of electron–hole recombination often results in low quantum yields and poor efficiencies in photocatalytic reactions [3]. These fundamental problems prevent practical applications of TiO_2.

To more effectively use solar energy, nonmetal or transition-metal doping into TiO_2 has been carried out to prepare visible-light active photocatalysts via band-gap narrowing [7–12]. Recent efforts have doped TiO_2 with nonmetallic species such as carbon (C), nitrogen (N), and sulfur (S), leading to spectral shifts toward the visible region [10–14]. Band structure calculations for nonmetal-doped TiO_2 suggested that oxygen sites were substituted by C, N, and S atoms, leading to a valence band shift through mixing of the 2*p* orbitals of both elements, and thus narrowing of the TiO_2 band-gap [15–17]. Therefore, nonmetal-doped TiO_2 is promising for the elimination of environmental pollutants in air or in water using visible-light [16,17]. Among nonmetallic elements, N doping has been widely investigated and some success has been achieved in extending the working spectrum of TiO_2 toward the visible-light range [18–21]. Various methods have been developed to prepare visible-light active N-doped TiO_2 (N-TiO_2) photocatalysts, such as annealing under a N_2 or NH_3 flow at high temperature (above 550 °C) [22,23], decomposition of nitrogen-organic precursors [24], sol–gel methods [25,26], ion implantation [27–29], and thin film deposition [30]. Most of these techniques generally require high temperatures or complicated and expensive equipment. Therefore, new strategies for preparing N-TiO_2 photocatalysts, such as ion implantiation [31], sol–gel processing at low temperature [32], hydrothermal synthesis [33], and plasma treatment [34,35], have been proposed. However, the synthesis of N-doped TiO_2 photocatalysts using a simple and room-temperature method remains a challenge for large-scale applications.

To improve visible-light photocatalysis in TiO_2 photocatalysts, numerous studies have examined the enhancement of the hydrophilicity of TiO_2 surfaces by various methods, including UV, acid, and plasma treatments [36–38]. Increased hydrophilicity on TiO_2 surfaces could expand the use of this technology in many practical applications, such as energy storage, water/air purification, and antimicrobial agents [37–39]. In this study, we report the synthesis of nanoporous N-TiO_2 with an anatase crystalline structure by modified sol–gel processing and ultrasound irradiation at room temperature (RT), without thermal treatment. In addition, the N-TiO_2 was irradiated with visible-light to improve its surface hydrophilicity. Visible-light irradiated N-TiO_2 (*N-TiO_2), with high crystallinity (pure anatase crystalline) and a large surface area (489.9 $m^2\,g^{-1}$), exhibited very high photocatalytic activity toward the oxidation of azo dyes [reactive black 5 (RB 5) and rhodamine B (Rho B)], and efficient sterilization (or killing) of bacteria [Gram-negative *Escherichia coli* (*E. coli*) and Gram-positive *Staphylococcus aureus* (*S. aureus*)] under visible-light irradiation. The photocatalytic and antibacterial activities of the *N-TiO_2 samples were higher than those of commercial 5-nm anatase TiO_2 (5 nm a-TiO_2), undoped TiO_2 (TiO_2), and N-TiO_2 photocatalysts.

2. Experimental

2.1. Synthesis of TiO_2 photocatalyst

Titanium *n*-butoxide [TBOT; $Ti(OCH_2CH_2CH_2CH_3)_4$, 97%], dodecyltrimethylammonium bromide [$CH_3(CH_2)_{11}N(CH_3)_3Br$], isopropanol [IPA; $(CH_3)_2CHOH$, 99.7%] and urea [$CO(NH_2)_2$] were used as received from Aldrich (St. Louis, MO, USA). In a typical synthesis, TBOT (0.056 mol) and dodecyltrimethylammonium bromide (0.01 mol) were dissolved in deionized water (1000 mL) and the mixture was vigorously stirred for 5 min at RT. After aging for 6 h, the white precipitate was filtered, washed five times with deionized water solution, and dried under air at RT. Then, dried TiO_2 powder (20 g; as grown TiO_2) was mixed with deionized water (1000 mL) and treated with high-intensity ultrasound at a frequency of 20 kHz, which was applied from the top of the glass reactor using a Sonics & Materials, Inc. (Newtown, CT, USA) VC 750 ultrasonic generator (13-mm diameter high-intensity probe, amplitude 50%) [40]. Ultrasound irradiation was applied for 40 min, with the electrical energy input maintained at 100 W cm^{-2}. Ultrasonic irradiation promotes the growth and collapse of gas bubbles (cavitation), leading to the temperatures around 5000 K, pressures of roughly 1000 atm, and heating and cooling rates above 10^{10} K/s [40]. The temperature of the mixture (TiO_2/water solution) increased from 25 °C to 42 °C for 40 min of ultrasound irradiation. The mixture was filtered, the resultant TiO_2 powder was washed several times with deionized water, and dried under vacuum at RT.

2.2. Synthesis of visible-light irradiated nitrogen-doped TiO_2 (*N-TiO_2) photocatalyst

TiO_2 powder (20 g) was dispersed in 8 wt% urea/IPA solution (1000 mL, 50:50 urea: IPA) and vigorously stirred for 10 min at RT. Ultrasound irradiation was applied for 40 min, maintaining the electrical energy input at 100 W cm^{-2}. The orange-red TiO_2 powder was filtered, washed five times with deionized water, and dried under air at RT. These samples were irradiated using a solar simulator (source: 150 W Xe lamp, SCHOTT, USA; humidity: 52–58%) over 1 h.

2.3. Characterization

The crystalline structures of the 5 nm a-TiO_2, as-grown TiO_2, TiO_2, N-TiO_2, and *N-TiO_2 photocatalysts were investigated by X-ray diffraction (XRD, Rigaku RDA-γA X-ray diffractometer, Tokyo, Japan) using Cu Kα radiation with a nickel filter. The morphologies and size distributions of the as-grown TiO_2, TiO_2, N-TiO_2, and *N-TiO_2 photocatalysts were evaluated by field-emission scanning electron microscopy (FE-SEM, Hitachi S-4700, Tokyo, Japan) and high-resolution transmission electron microscopy (HR-TEM, JEOL JEM 2200, Tokyo, Japan). Before analysis, the samples were placed on the surfaces of copper grids and dried under ambient conditions. The wettabilities and surface energies of the TiO_2 samples were evaluated by measuring the contact angles of liquid drops (deionized water, ethylene glycol, and *n*-hexane) formed on the surface of visible-light irradiated samples using a contact angle measurement system (Dataphysics OCA10, Germany). The TiO_2 samples were pressed in pellet shape (~25 mm diameter and about ~5 mm thickness) by uniaxially applying a pressure of 260 MPa in hydraulic press machine at room temperature. Five independent determinations at different sites on three samples were averaged. The surface energies of the TiO_2 samples were calculated using the extended Fowkes' equation [36]. The BET surface areas, pore volumes, and pore diameters of the as-grown TiO_2,