



N-TiO₂-coated polyester filters for visible light–Photocatalytic removal of gaseous toluene under static and dynamic flow conditions



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ABSTRACT

The present work aims to utilize N-TiO₂ coating for decontamination of gaseous pollutants under normal room light irradiation. N-TiO₂ nanoparticles were prepared by incomplete thermal oxidation of TiN at different temperatures to achieve self-doping of TiO₂ to improve simultaneously the structural, morphological, and electronic properties of conventional TiO₂ photocatalyst. The thermal evolution of TiN to oxygen-rich titanium oxynitride (N-TiO₂) and subsequently TiO₂ at different temperatures is characterized systematically by different tools including XRD, TEM, XPS, UV–vis diffuse reflectance and SPV responses. The synthesized N-TiO₂ was coated onto polyester filters using a facile spray coating method. The excellent photocatalytic performance was successfully demonstrated on mineralization of gaseous toluene with fluorescent light irradiation under both static and dynamic flow conditions in a comprehensive custom-built photocatalytic test system. Therefore, it shows promising potential to be utilized in practical air purification applications.

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1. Introduction

Since the discovery of photocatalytic water splitting on TiO₂ electrodes in 1972 [1], titanium dioxide (TiO₂) as the most practical and prevalent photocatalyst has been the target for extensive research due to its various advantages including high reactivity, chemical stability, robustness against photocorrosion, low toxicity and low cost. However, UV light excitation (<385 nm) is required because of the large bandgap of TiO₂ (3.0–3.2 eV), limiting its practical applications. A lot of efforts have been therefore devoted to increase the visible light sensitivity of TiO₂ in order to harness the abundant visible light portion (400–700 nm) in solar light (ca. 45%) as well as relatively weak room light.

One of the most efficient methods is to dope TiO₂ with non-metals such as C, N, F, and S [2–5], which are often referred to as the second generation photocatalysts. These anion dopants will lead to band gap narrowing or formation of localized mid bandgap states,

effectively extending the absorption threshold of TiO₂ into visible light range. N-TiO₂ is the most widely investigated anion-doped TiO₂ since the report of substitutional nitrogen doping into oxygen sites by Asahi in 2001, exhibiting significant red shift from the UV to the visible spectral range up to 500 nm [2]. On the basis of electronic band structure modification, the sufficient overlapping of N 2p states with the O 2p states at valence band maximum can enable efficient bandgap narrowing for visible light absorption [6]. S doping could produce similar bandgap narrowing, yet it is difficult to be incorporated into O sites in TiO₂ due to its large ionic radius. C or P doping on the other hand may introduce states too deep within the gap, which might serve as recombination centers. Therefore, N-TiO₂ remains as the leading visible light sensitive photocatalyst.

Conventional approaches to produce N-TiO₂ include nitrification of TiO₂ by sol-gel [5,7], sputtering and ion-implantation [2,8], chemical vapor deposition [9], and heat treatment in N₂ or NH₃ [10,11], which usually involves complex reactions. Alternatively, N-TiO₂ can also be obtained through oxidation of N-containing precursors [12,13]. In particular, oxidation annealing of TiN in O₂ flow has been reported by Morikawa and Asahi et al. as early as in 2001 to produce N-TiO₂, which appears as an environmentally

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benign facile synthesis approach without utilizing harmful reagents or generating toxic byproducts. However, systematic study of thermal evolution of TiN to oxygen-rich titanium oxynitride (N-TiO₂) and subsequently TiO₂ at different temperatures is lacking to correlate with its photocatalytic performance. In addition, little is known about the photocatalytic properties of N-TiO₂ by oxidation of TiN under room light irradiation, especially in coated form for gaseous pollutants removal to simulate the actual usage in practical air purification.

In the present work, preparation of N-TiO₂ is studied systematically by thermal oxidation of TiN at 350–600 °C in air for two hours. The thermal evolution from TiN to anatase and rutile mixed phase of TiO₂ was studied by XRD and TEM observations. The binding states and surface stoichiometry of the nitrogen in the TiO₂ lattice were investigated using X-ray photoelectron spectroscopy (XPS). In addition, surface photovoltage (SPV) for N-TiO₂ by oxidation of TiN were recorded for the first time to correlate with the charge-separation efficiency. The synthesized N-TiO₂ was coated onto polyester filters using a facile spray coating method, with silica colloidal silica as binders to impart adhesion. The visible light photocatalytic performance of the coated samples was demonstrated on removal of gaseous toluene under both static and dynamic flow conditions in a comprehensive custom-built photocatalytic test system.

2. Experimental

2.1. Photocatalyst preparation

N-TiO₂ was synthesized by controlled oxidation of TiN. The nano-sized TiN powders (97%, oxygen < 1.0%, Hefei Kaier) with an average particle size of 20 nm was produced by the RF induction thermal plasma process using titanium tetrachloride as the precursor. Typically, 2 g of the as-purchased TiN powders was bestrewed on an alumina combustion boat (9 cm, Coorstek) and heated in a muffle furnace (F62700, Barnstead) at 350–600 °C for 2 h in air to achieve different nitrogen:oxygen and anatase:rutile ratios. The temperature was ramped up at 10 °C/min, and allowed to cool naturally overnight to room temperature. The commercial TiO₂ P25 (≥99.5%, Evonik) was used as received without further purification. It serves as a reference to evaluate the performance of the synthesized N-TiO₂.

2.2. Photocatalyst characterization

The crystallographic structures were studied using a X-ray diffractometer (D5005, Siemens) with an X-ray source of 1.54 Å Cu K α operating at 40 kV and 40 mA. The specific surface area (SSA) of the N-TiO₂ nanoparticles was measured at liquid nitrogen temperature (77 K) with the physisorption analyzer (ASAP 2020, Micromeritics) based on the Brunauer, Teller and Emmet (BET) model. The powder samples were degassed at 200 °C in vacuum for 2 h before SSA measurement. The effect of thermal oxidation on the morphology and structure of the TiN was observed using a transmission electron microscopy (TEM, JEM-2100F, JEOL). The TEM samples were prepared by sonication of the powders in ethanol for 15 min and subsequently the dispersion was dropped onto carbon copper grids. Chemical states analysis was performed with X-ray photoelectron spectrometer (XPS, Axis-Ultra, Kratos) equipped with monochromatic Al K α X-ray source (KE = 1486.6 eV, 15 kV, 150 W). All XPS spectra were referenced to the C1s peak of adventitious hydrocarbon contamination located at 284.8 eV to correct the charging effect. Peak fittings of the XPS data were accomplished with a Shirley-type background subtraction using the spectra deconvolution software CasaXPS. Diffuse reflectance spectra were recorded in the range of 240–800 nm in reference to

barium sulphate (BaSO₄) using a UV–vis spectrometer (UV-2450, Shimadzu) fitted with a multipurpose sample compartment (MPC-2200, Shimadzu). A Kubelka–Munk (KM) transformation was done on the reflectance data to obtain the absorbance spectra for red shift observation [14].

2.3. Surface photovoltage responses (SPV)

SPV response was characterized by measuring the change in contact potential difference (Δ CPD) of the sample with respect to the reference probe in dark and upon irradiation. The measurement system consists of a commercial UHV Kelvin probe unit (KP Technology Ltd.) incorporated with high-power LED sources (Mightex LED) with switchable wavelength from UV (365 nm) to near infrared (850 nm) through a quartz window. The maximum power at its output for $\lambda = 455$ nm is 350 mW. The SPV particulate film was prepared by dispersing the powders in propylene carbonate binder and coated onto the FTO glass by doctor-blade method. All samples were kept in dark for more than 16 h to stabilize their surface charges, followed by illumination for 700 s.

2.4. Photocatalytic coating preparation

The photocatalytic coatings were prepared by spraying pre-dispersed photocatalysts suspension onto polyester filters. The coating suspensions were prepared using 50 g/L of each as-prepared or as-received photocatalyst in 80 vol% distilled water and 20 vol% colloidal silica as binders (Aldrich, LUDOX AS-40). The polyester substrates used in this study are nonwoven dry polyester fabrics, with a typical filter thickness of 5 mm and overall packing density of 0.055 g/cm³. These substrates were cut into sizes of 200 mm \times 300 mm and 50 mm \times 100 mm to be fitted into batch and dynamic reactors, respectively. A Navite F-75G spray gun (Navite, China) was then used for spray coating, with nitrogen as the carrier gas under a pressure of 65 psi and a spray distance of 150 mm for 10 passes. An interval of 15 min was taken in between passes using a blow drier to evaporate water. The spray-coated substrates were finally cured at 60 °C for 3 h to stabilize the coatings. The substrate was weighed by a digital analytical balance (readability of 0.0001 g, Mettler–Toledo, Switzerland) before and after coating. The average net loading of the powders was ca. 0.65 g and 0.05 g for static and dynamic flow tests, respectively.

2.5. Photocatalytic degradation of gaseous toluene

Toluene as a major indoor volatile organic compound was chosen as the probe pollutant to evaluate the photocatalytic performance of the synthesized N-TiO₂ nanoparticles coatings. The schematic of the simplified experimental setup is illustrated in Fig. 1. In general, the test system consisted of four parts: (1) a test gas supply, (2) two batch photoreactors and three dynamic photoreactors enabling the evaluation of photocatalytic test pieces under both static and continuous flow conditions, (3) housing for the photoreactors with different light sources, and (4) gas sampling and analysis configurations. The pollutant gas was generated by evaporating the liquid source and brought into the photoreactors by the diluting air. Specifically, the liquid toluene (>99%, Fisher) in a stainless steel syringe (50 mL, KD Scientific) was injected into a heating chamber (HC1) at a constant infusion rate as controlled by a syringe pump (SP1) and it would get vaporized at around 50 °C. At the same time, compressed dry air (CDA) would go through a zero air gas generator (ZAG, ZA300, Peak Scientific Instrument) to produce a constant flow of zero grade air with a hydrocarbon content (as methane) of less than 0.1 ppm. The zero air would serve as both diluting and carrier gas for the vaporized pollutant to achieve a first stage dilution concentration of ca. 2000 ppm by

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