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N-TiO₂-Coated Polyester Filters for Visible Light-Photocatalytic Removal of Gaseous Toluene under Static and Dynamic Flow Conditions

Li Zhang ^{a, b*}, Pei Yun Tan ^b, Chiew Keat Lim ^a, Xiao Guo ^b, Man Siu Tse ^{a, b}, Ooi Kiang Tan ^{a, b} and Victor W. C. Chang ^{c, d}

^a Temasek Laboratories @ Nanyang Technological University, 50 Nanyang Drive, Singapore 637553

^b Nanomaterials Lab, School of Electrical & Electronic Engineering, Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798

^c Division of Environmental and Water Resources, School of Civil and Environmental Engineering, Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798

^d Nanyang Environment and Water Research Institute, Nanyang Technological University, 1 Cleantech Loop, CleanTech One #06-08, Singapore 637141

* Corresponding author. Tel: (+65)98207258. Email address: zh0012li@e.ntu.edu.sg.

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.

Keywords

N-TiO₂; Coating; Photocatalysis; Visible light; Reactors; Toluene;

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 TiO_2 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 TiO_2 into visible light range. N- TiO_2 is the most widely investigated anion-doped TiO_2 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 TiO_2 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- TiO_2 remains as the leading visible light sensitive photocatalyst.

Conventional approaches to produce N- TiO_2 include nitrification of TiO_2 by sol-gel [5, 7], sputtering and ion-implantation [2, 8], chemical vapour deposition [9], and heat treatment in N_2 or NH_3 [10, 11], which usually involves complex reactions. Alternatively, N- TiO_2 can also be obtained through oxidation of N-containing precursors [12, 13]. In particular, oxidation annealing of TiN in O_2 flow has been reported by Morikawa and Asahi *et al.* as early as in 2001 to produce N- TiO_2 , which appears as an environmentally 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- TiO_2) and

subsequently TiO_2 at different temperatures is lacking to correlate with its photocatalytic performance. In addition, little is known about the photocatalytic properties of N- TiO_2 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- TiO_2 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 TiO_2 was studied by XRD and TEM observations. The binding states and surface stoichiometry of the nitrogen in the TiO_2 lattice were investigated using X-ray photoelectron spectroscopy (XPS). In addition, surface photovoltage (SPV) for N- TiO_2 by oxidation of TiN were recorded for the first time to correlate with the charge-separation efficiency. The synthesized N- TiO_2 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- TiO_2 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 were

bestrewed on an alumina combustion boat (9 cm, Coorstek) and heated in a muffle furnace (F62700, Barnstead) at 350-600 °C for 2 hours 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, Simens) 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 hours 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 minutes 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, 150W). 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 (BaSO_4) 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 (ΔCPD) 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 hours to stabilize their surface charges, followed by illumination for 700 seconds.

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 × 300 mm and 50 mm × 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 hours 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 Figure 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 setting the flow rate of the mass flow controller **MFC5**. The diluted pollutant gas would undergo second stage dilution by homogenizing with the humidified zero air in a mixing chamber (**MIX**) with a temperature/humidity/pressure probe. The final concentration of the pollutant in **MIX** would be controlled by **MFC6** and **MFC7** while the relative humidity of the gas stream is determined by the water infusion rate set by another syringe pump (**SP2**). The gas would be supplied into the photoreactors (**PR1-PR3** or **BR1-BR2**) with different test pieces and its concentration would be monitored with a gas chromatography (**GC**, Clarus 600, Perkin Elmer) with flame ionization detector (FID). In the batch test, once the desirable toluene concentration of 10 ppm and humidity level of 70% are established, the two 6 L batch reactors (**BR1** and **BR2**) were pressurized with the toluene contaminated gas by closing the exit valves **BP4** and **BP5** to 30 psi and then the inlet valves (**BP2** to **BP3**) were closed before the photocatalytic study. In the dynamic test, 10 ppm toluene with 40% RH was supplied into the three dynamic reactors continuously at a feeding rate of 50 ml/min, as controlled by the mass flow controllers **MFC1-MFC3**. Seven pieces of fluorescent light tubes (**FL**, T5 13W/ 765, OSRAM, emission spectrum shown in the supporting information S1) were placed above the reactors with UV-block filters (GG400, Schott) in between to cut out the UV light less than 400 nm and the resultant visible light

illuminance was adjusted to 10000 lux on the sample surface. The formation of CO₂ as a final mineralization product was monitored with customized methanizer + FID path inside the GC to quantitatively compare the photocatalytic performance. Each test was repeated with the same sample at least twice to ensure the repeatability and reusability.

3. Results and Discussions

3.1 Thermal Evolution from Titanium Nitride to Titanium Dioxide

Based on the XRD spectra in Figure 2, a NaCl-type, face-centred cubic crystal structure (JCPDS 38-1420) was observed in the as-received TiN powder, which remained as the only phase up to 350°C. The powder transformed into anatase TiO₂ (JCPDS 21-1272) at 400°C with some traces of TiN cubic structure remaining. At 450°C, TiN phase completely disappeared and peaks for rutile TiO₂ (JCPDS 65-1119) were detected, signifying the formation of mixed phase TiO₂ due to the transition of anatase phase to rutile structure. Therefore, for N-TiO₂ formation from direct oxidation of TiN in air, the minimum annealing temperature should be 450°C in order to eliminate any residual TiN phase. According to the XRD spectra, the phase composition and crystallite size were estimated and summarized in Table 1. With increasing annealing temperature from 450 °C to 600 °C, the weight ratio of rutile TiO₂ increased from 0.16 to 0.44, resembling the phase structure of the highly efficient P25 TiO₂ with rutile content of ca. 30%. The crystallite size of the TiN precursor was estimated to be ca.14.38 nm based on the strongest peak at $2\theta = 42.6^\circ$. Upon annealing, the crystallite sizes of TiN followed a trend of first-decrease and

then-increase with increasing temperature, consistent with the change in primary particle sizes estimated from the measured BET surface area. This phenomenon could be attributed to the grain cracking of TiN, which allows renucleation of TiO₂ with much smaller crystallite size [15]. Once the recovery and recrystallization were completed, grain growth was resumed to further reduce the internal energy. A significant increase in grain size and reduction in BET surface area was observed at 600 °C due to fast particle sintering at elevated temperature.

Further insights into the effect of oxidation on the morphology and structure were obtained by TEM observations as shown in Figure 3. The pristine TiN nanoparticles have uniformly distributed particle size of less than 50 nm (Figure 3a). HRTEM image in Figure 3b further shows a clear fringe spacing of 0.21 nm, corresponding to the *d*-spacing of the (200) lattice plane of the cubic TiN structure [16], which is the plane of the lowest surface energy and thus the preferred orientation. This well-crystallized TiN phase in the core was surrounded by a thin amorphous overcoat. This overcoat layer is believed to be oxynitride phase, TiN_xO_y formed after TiN exposure to air which was also observed by Jung et al. on sputtered TiN samples [17]. After annealing at 500 °C, the particle size did not increase significantly in good agreement with the BET surface area measurements. Meanwhile, the amorphous outer layer had reduced significantly, and a selected area electron diffraction (SAED) pattern of polycrystalline nature was revealed in Figure 3d. Well-crystallized grains with lattice spacing of 0.35 nm can be identified as anatase (101) planes of TiO₂, which is consistent with XRD analysis.

3.2 Chemical States and Surface Stoichiometry Study

The chemical states of the elements were investigated by XPS analysis. Figure 4a shows the Ti 2p XPS spectra for TiN annealed at 350 °C, which consisted of three pairs of doublet peaks due to inherent orbital splitting. The peak centered at 458.6 ± 0.2 eV with highest intensity could be assigned to O-Ti-O bonds while the one centered at 455.4 ± 0.1 eV with lowest intensity was due to N-Ti-N bonds from bulk titanium nitride species [18]. The middle peak centered at 456.9 ± 0.1 eV could be attributed to a combination of Ti-N-O bonds from the oxynitride species which formed due to residual oxygen after the TiN preparation process [19] and shake-up satellite peaks due to interband transitions such as those observed by Strydom et. al [20] using electron energy loss spectroscopy (EELS). The intense O 1s peak at ca. 530.1 eV in Figure 4b originates from the O-Ti-O bonds, indicating the formation of bulk TiO₂. The middle peak at 531.1 eV could be assigned to Ti-N-O bond in oxynitride phase [19] while another relatively lower peak at ca. 532 eV was usually assigned to surface adventitious species such as hydrocarbon (C-H), carbonate species (C-O, C=O) and adsorbed water (OH_{ads}) bonds due to contamination from environment during characterization. For the N 1s spectra which is of our particular interest, the main peaks at ca. 396.0 eV and 397.3 eV could be attributed to N-Ti-O peak due to the presence of oxynitride phase [18] and N-Ti-N bonds due to nitrogen in TiN environment [18, 19]. Besides these two main peaks, there was a small peak detected at higher binding energy of ca. 402 eV, which has been reported to be chemisorbed N₂, also denoted as γ -N₂, released during the oxidation of TiN and trapped underneath the oxynitride layers [21]. For annealing temperature at 400 °C

and above, the overall N 1s peak intensity diminished quickly and became zero from 600°C onwards (Figure 4d) due to the parabolic oxidation rate at high temperature [22]. The spectra also had slightly different profiles with a new peak centred between 399.7-400.0 eV observed, which probably originated from interstitially-doped nitrogen atoms in TiO₂ environment and would contribute to the formation of localized mid-bandgap N 2p energy states. The fact that this interstitial nitrogen species were only detected at 400 °C and above is consistent with the XRD analysis that anatase TiO₂ was only formed at this temperature range. N-Ti-N and N-Ti-O bonds can still be observed due to a small amount of residual, incompletely oxidized TiN phase.

The atomic concentrations for Ti, O and N were calculated and depicted in Figure 5 with respect to annealing temperature after omitting all surface adventitious species including C 1s peaks and OH_{ads}. The pristine TiN was oxygen-rich on the surface due to prolonged exposure to air before annealing. The nitrogen content remained at 21.5% upon annealing up to 250 °C, beyond which dropped sharply to 1.89% at 400°C due to the fast oxidation process. At 450 °C, 500 °C and 550 °C, the nitrogen contents were 1.43%, 1.34% and 0.52%, respectively. It was also noticed that the O/Ti atomic ratio changed from non-stoichiometric of 1.87 to near stoichiometric values of 2.00 from 400 °C to 600 °C due to diminished nitrogen content.

3.3 Optical Properties

The UV-vis absorption spectra of TiN annealed at 450-600 °C are presented in Figure 6 in comparison to P25 TiO₂. All samples have improved absorbance in both UV and visible-light regions as compared to P25. With increased annealing

temperature, the fundamental absorption edge for samples annealed at 450 °C, 500 °C and 550 °C can be extrapolated to approximately 400 nm, similar to that of P25 while the absorption edge for TiN annealed at 600 °C red shifted into the visible light range. Due to the absence of nitrogen peak in XPS analysis at 600 °C, this shift is more likely to be attributed to the increase of rutile content, which has a bandgap of 3.05 eV corresponding to a wavelength of 407 nm [23]. Absorption tails extending up to 500 nm were also observed for samples annealed from 450°C to 550°C with absorbance decreasing with annealing temperature due to decreased nitrogen content as evidenced in XPS analysis. As such, these absorption tails should come from light absorption from localized midgap N 2p states introduced by the nitrogen dopants. These acceptors states are widely agreed to lie slightly above the valence O 2p states [8, 10].

3.4 Surface Photovoltage (SPV) Study

Kelvin Probe based SPV measures the contact potential change as a result of illumination. Different from diffuse reflectance absorption spectra, the magnitude of the surface photovoltage does not only depend on the number of electron-hole pairs generated by photon absorption, but also the diffusion of these carriers to surface states which in turn, also depends on the charge separation efficiency. A larger surface photovoltage signal indicates that more charge carriers can diffuse to the particle surface to cause a larger contact potential difference. As shown in Figure 7, TiN annealed at 500 °C showed the highest SPV value of 180 mV, which is consistent with the XPS analysis that the 500 °C oxidized sample had the highest amount of nitrogen dopants in interstitial sites allowing absorbing visible-light photon to generate electron-hole pairs. By further increasing the oxidization temperature up to

600 °C, the SPV magnitudes of the samples deteriorated due to reduced nitrogen content and thus lower visible-light absorption. Upon removal of illumination, charge decay for all samples was observed, relating to their surface electrical properties for charge diffusion and electron-hole pair recombination. The decay rate was found to decrease with increasing annealing temperature from 450 °C to 600 °C. From XPS analysis, while the nitrogen content decreased with oxidization temperature, the surface oxygen stoichiometry became closer to the stoichiometric TiO₂ composition. As a result, it is expected that the surface resistance of the powders increased with annealing temperature, suppressing the surface charge diffusion, causing the slower decay of SPV response.

3.5 Photocatalytic Degradation of Gaseous Toluene

The photocatalytic performance of the synthesized N-TiO₂ prepared at 450-550 °C was evaluated on 10 ppm toluene in a 6-L batch reactors under normal fluorescent light irradiation by filtering away the UV portion. The amount of CO₂ evolution was monitored to represent the degree of mineralization as shown in Figure 8. Within the 6 hours of experimental duration, the best performance was achieved in the presence of TiN annealed at 500 °C by generation of ca. 28 ppm CO₂, corresponding to mineralization of 4 ppm toluene or 40% mineralization efficiency based on carbon balance. Based on the first order reaction kinetics, total mineralization of toluene was expected to be completed within 15 hours and much higher photocatalytic efficiency was also expected with stronger light irradiation. The optimized performance could be attributed to the best balance among the surface area, ratio of anatase/rutile phase, defects states, and most importantly the amount of interstitial nitrogen dopant content

contributing to the formation of N 2p states above valence O 2p band that can absorb visible-light photons. At 450 °C, nitrogen remaining was mostly trapped as N₂ molecules instead of at interstitial dopant level, and a significant percentage still remained in TiN and oxynitride environments. Furthermore, the oxygen vacancies detected by XPS could form trapping and recombination sites that hinder charge transfer to particle surface for photocatalytic reactions. Its lower surface photovoltage magnitude in SPV analysis is a good indication for the faster recombination rate, which resulted in relatively poorer performance as compared to sample annealed at 500 °C. TiN annealed at 550 °C had the least interstitial nitrogen and its photocatalytic performance was the poorest, comparable to the market leader P25 with similar anatase/rutile ratio. Overall, satisfactory performance was achieved on N-TiO₂ synthesized by thermal oxidation of TiN at 450-550 °C.

Under continuous flow of toluene at 50 ml/min, the photocatalytic performance followed similar order as in the batch test. As shown in Figure 9, minimal CO₂ concentration was detected in the inlet and control sample in the absence of any photocatalyst under all irradiation conditions. Upon visible light irradiation, TiN annealed at 500 °C exhibited the best photocatalytic performance followed by that annealed at 450 °C, 550 °C and P25. However, it should be noted that the highest mineralization efficiency of 4% in the presence of N-TiO₂ annealed at 500 °C is still rather low as compared to the static condition, due to the short residence time of 26.67 seconds over a small area of 5 cm × 10 cm on the photocatalytic test piece, where limited gas phase mass transfer and the transport of pollutants to the catalyst surface takes place [24]. For actual air treatment, it is expected that the mineralization

rate can be enhanced significantly by dispersing these photocatalysts over large interior surface such as wall, tiles, furniture to allow the air bound pollutants to have higher probability to be captured and destroyed by the active components. The cleaning of the air will take action as long as the coated area is illuminated by the normal indoor lighting without additional energy input.

4. Conclusions

Oxygen-rich titanium oxynitride (N-TiO₂) was successfully synthesized by thermal oxidation of TiN at 450 °C-550 °C for 2 hours in air. Based on XRD study and TEM observation, the formation of mixed phase TiO₂ was found to start from an amorphous oxynitride overcoat surrounding well-crystallized TiN core that formed into well-crystallized TiO₂ upon annealing. XPS study confirmed the existence of beneficial nitrogen-dopants in interstitial position which allowed visible-light absorption. Meanwhile, surface photovoltage spectra revealed the superior charge separation which is believed to be contributed by the optimum anatase to rutile ratio. The nano-sized powders showed visible-light absorption up to 525 nm with enhanced gaseous toluene oxidation under visible-light illumination in comparison with P25 TiO₂. The photocatalysts were spray coated onto polyesters for mineralization of gaseous toluene under both static and dynamic flow conditions. In particular, the best photocatalytic performance was achieved with TiN annealed at 500 °C, possibly due to the best balance among the surface area, ratio of anatase/rutile phase, defects states, and the amount of interstitial nitrogen dopant content. The excellent visible light photoactivity does not only render the synthesized N-TiO₂ nanoparticles promising

photocatalysts for indoor environmental remediation, but also may stimulate other solar applications such as water splitting and artificial photosynthesis.

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Figure 1. Schematic representation of the experimental setup including two batch reactors and three dynamic reactors.

Figure 2. XRD spectra of nano-sized TiN powder at different annealing temperatures.

Figure 3. HRTEM images for (a)-(b) TiN and (c)-(d) TiN oxidized at 500 °C.

Figure 4. XPS spectra of (a) Ti 2p, (b) O 1s (c) N 1s in TiN annealed at 350 °C and (d) N 1s core-level spectra of TiN oxidized at 400-600 °C.

Figure 5. Atomic concentration of TiN at different annealing temperatures.

Figure 6. Effect of annealing temperature on the light absorption of TiN powders.

Figure 7. Surface potential change of TiN powder annealed at different temperatures and P25 under blue LED illumination ($\lambda = 455$ nm).

Figure 8. Evolution of CO₂ during the photocatalytic oxidation of 10 ppm toluene in batch reactor.

Figure 9. Evolution of CO₂ during the photocatalytic oxidation of 10 ppm toluene in dynamic reactor.

Table 1 Summary of physicochemical properties of TiN annealed at different temperatures

Annealing temperature (°C)	Rutile content ^a	Crystallite size (nm) ^b		BET SSA (m ² /g)	Particle size (nm) ^c	Nitrogen content (atm%)	SPV (mV)
		Anatase	Rutile				
450	0.16	9.7	10.9	33.0	46.6	1.43	160
500	0.22	11.2	12.5	32.4	47.5	1.34	180
550	0.29	11.6	12.4	29.8	51.6	0.52	130
600	0.44	13.5	14.0	22.0	69.9	0	90

^a Rutile content = $(1 + 0.8I_A/I_R)^{-1}$ where I_A and I_R are the X-ray intensities of the anatase and the rutile peaks at Bragg peaks $2\theta = 25.3^\circ$ and 27.5° respectively

^b Estimated with Scherrer Formula $D = 0.94\lambda/\beta\cos\theta$

^c $d_{BET} = 6/S_{BET}\rho$ assuming the particles are roughly spherical, $\rho_{TiO_2 \text{ anatase}} = 3.90 \text{ g/cm}^3$