Synthesis of N-Doped TiO$_2$ for Efficient Photocatalytic Degradation of Atmospheric NO$_x$

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Abstract: Titanium oxide (TiO$_2$) is a potential photocatalyst for removing toxic NO$_x$ from the atmosphere. Its practical application is, however, significantly limited by its low absorption into visible light and a high degree of charge recombination. The overall photocatalytic activity of TiO$_2$ remains too low since it can utilize only about 4–5% of solar energy. Nitrogen doping into the TiO$_2$ lattice takes advantage of utilizing a wide range of solar radiation by increasing the absorption capability towards the visible light region. In this work, N-doped TiO$_2$, referred to as TC, was synthesized by a simple co-precipitation of tri-thiocyanuric acid (TCA) with P25 followed by heat treatment at 550 degrees C. The resulting nitrogen doping increased the visible-light absorption and enhanced the separation/transfer of photo-excited charge carriers by capturing holes by reduced titanium ions. As a result, TC samples exhibited excellent photocatalytic activities of 59% and 51% in NO oxidation under UV and visible light irradiation, in which the optimum mass ratio of TCA to titanium ions. As a result, TC samples exhibited excellent photocatalytic activities of 59% and 51% in NO oxidation under UV and visible light irradiation, in which the optimum mass ratio of TCA to P25 was found to be 10.

Keywords: N-doped TiO$_2$; precipitation; NO$_x$ removal

1. Introduction

Atmospheric pollution resulting from photochemical oxidants, such as nitrogen oxides (NO$_x$: NO+NO$_2$) and ozone, has been considered one of the critical concerns in urban areas. [1]. NO$_x$, a by-product resulting from fossil fuel incineration and photochemical conversion in nature, is mainly considered a dominant contributor to environmental problems such as photochemical smog, acid rain, haze, etc. [2,3]. The atmospheric NO$_x$ concentration (annual mean concentrations of 0.01–0.05 ppm in urban areas over the world [4]) has drastically increased over the past few decades due to industrial genesis and automobile development [2]. NO$_x$ has stimulating effects on the environment, human and animal health, and plant vegetation [5]. Consequently, over the past few decades, the demand to mitigate the detrimental effects of NO$_x$ has increased in light of sustainable climate policy, and this has inspired increased focus on NO$_x$ efficacy. Therefore, researchers
have manifested various schemes such as direct decomposition [6], selective catalytic/non-catalytic reduction [7], solid–liquid adsorption [8], plasma-assisted catalytic reduction [9], and photocatalytic oxidation (PCO) for effective removal of NO\textsubscript{x} from the atmosphere. However, most of those propositions are not commercially feasible for NO\textsubscript{x} removal at low concentration levels and require intricate devices, engineering, or relatively high temperatures.

Among various approaches, PCO is a potential and cost-effective method to manage atmospheric pollutants [10]. The PCO of NO\textsubscript{x} is an effective process due to its ability to use enormous, inexhaustible solar energy, moderate reaction conditions appropriate for cheap and large-scale application [11,12]. TiO\textsubscript{2} has gained significant attention as a photocatalyst with the breakthrough of photocatalytic water splitting capability. What is more, TiO\textsubscript{2} features a strong photocatalytic oxidation competence, photostability, non-toxicity, and cost-effectiveness [13]. Usually, from theoretical and experimental studies, it has been demonstrated that the dominant anatase facets have better photoactivity than rutile [14]. Under UV light irradiation, TiO\textsubscript{2} generates electrons and holes in the conduction band and valence bands, respectively, facilitating the oxidation-reduction (redox) reactions for pollutant degradation [15,16]. However, the photocatalytic activities of anatase TiO\textsubscript{2} are restricted by their large energy bandgap (~3.6 eV) and immediate recombination of photogenerated e\textsuperscript{−}/h\textsuperscript{+} pairs [17]. Consequently, typical TiO\textsubscript{2} primarily exhibits low quantum efficiency under UV irradiation with a wavelength of <387 nm. Therefore, TiO\textsubscript{2} can utilize a maximum of 4–5% of the solar radiation during photocatalysis [17], mostly wasted for recombination in their bulk phase. So far, researchers have proposed many strategies for the improvement of photocatalytic activity of TiO\textsubscript{2} in NO oxidation by varying their crystal phase [18], engineering the energy bandgap to shift its absorption edge into the visible region [19,20], increasing specific surface area via porosity introduction [21], and doping of anions such as nitrogen and carbon in TiO\textsubscript{2} [22–24].

In this study, nitrogen is considered to be an effective dopant because of its similar size (155 pm) to oxygen (152 pm) as well as similar ionization energy (first ionization energy 1402.3 kJ/mol) compared to oxygen (first ionization energy 1313.9 kJ/mol) [25]. N-doped TiO\textsubscript{2} also has an improved photocatalytic activity in the visible light region, similar to oxidation of CO, C\textsubscript{2}H\textsubscript{6}, and ethylene [26,27]. It is well established that the doping of nitrogen into the TiO\textsubscript{2} lattice produces a narrower band gap by coupling N 2p states with O 2p states and creates donor states over the valence band (VB). This process attenuates the energy band gap of TiO\textsubscript{2} and generates oxygen vacancy, both of which enhance the absorbance of visible light [28]. Therefore, in this study, N-doped TiO\textsubscript{2} powder was fabricated by a simple co-precipitation of TCA and TiO\textsubscript{2}P25, followed by calcination at 550 °C for 4 h in N\textsubscript{2} atmosphere. This is the novel strategy to synthesize N-doped TiO\textsubscript{2} from TCA as a nitrogen precursor. In general, the substitution of nitrogen with oxygen in TiO\textsubscript{2} happens above 675 °C under N\textsubscript{2} atmosphere using cyanamide, melamine, and melem as nitrogen sources. Nevertheless, in this study, using TCA lowers the temperature to 550 °C since the SH group acts as a leaving group, and at lower temperatures polycondensation takes place, which facilitates doping of nitrogen into TiO\textsubscript{2} [29,30]. The synthesized N-doped TiO\textsubscript{2} materials showed a pronounced ability to absorb visible light and improved the bandgap structure with more negative (0.73 eV) conduction band (CB) potential than O\textsubscript{2}/O\textsubscript{2}− potential of −0.33 eV for NO oxidation. Thus, with such a narrow energy bandgap and broad absorption ability of visible light, the synthesized N-doped TiO\textsubscript{2} materials exhibited enhanced photocatalytic oxidation of NO under both UV and visible light irradiation. This study governs a new method for fabricating N-doped TiO\textsubscript{2} for efficient photocatalytic degradation of noxious atmospheric NO\textsubscript{x}.

2. Results and Discussion

The crystal phase structure of the prepared materials was investigated using XRD. Figure 1a compares the XRD patterns of pure TiO\textsubscript{2} P25 and all the prepared N-doped TiO\textsubscript{2} materials (TCX; TC means N-doped TiO\textsubscript{2}, X is wt% of TCA on TiO\textsubscript{2}). It showed that
both the anatase phase (JCPDS21-1272) and the rutile phase (JCPDS21-1276) of TiO2 were present in pure TiO2 as well as N-doped TiO2 materials. This is consistent with the biphasic structure of commercial TiO2 P25. The XRD patterns also indicate that there were no other characteristic peaks from impurities. To further investigate N doping effects on crystallite size, the calculated crystal size of pure TiO2 P25 and the synthesized N-doped TiO2 are given in supporting information in Table S1. The crystal size of synthesized materials was determined from half-width of (101) peak using Scherrer’s formula. The crystallite size of pure TiO2 P25 was found at 16.60 nm [31]. The crystallite size increased up to 18.54 nm with doping of larger atomic radius nitrogen (N$^3$ – 170 Å) into oxygen (O$^2$ – 140 Å) [32]. In this study, though the shifting of peak position was not observed significantly, the crystallite size increased with nitrogen doping. This phenomenon can be explained by the fact that the nitrogen doping may sharpen the XRD peak by enhancing the growth rate of crystal and increase the crystallite size.

![Figure 1](image_url)

**Figure 1.** (a) XRD patterns and (b) FT-IR spectra of pure TiO2 P25 and the synthesized N-doped TiO2 materials (TCX; TC means N-doped TiO2, X is wt% of TCA on TiO2).

FT-IR spectra of pure TiO2 P25 and the synthesized N-doped TiO2 materials are illustrated in Figure 1b. The absorption peak in the region between 650 cm$^{-1}$ and 800 cm$^{-1}$ was identified for the Ti–O and O–Ti–O bond vibrations for both the N-doped TiO2 and pure TiO2 P25 [33]. The broad absorption peak between 3000 cm$^{-1}$ and 3600 cm$^{-1}$ was attributed to the N-H stretching vibration of the residual N-H group or O-H of absorbed H$_2$O [34]. The small absorption peak at 1050 cm$^{-1}$ for the N-Ti-O bond was observed for all the synthesized N-doped TiO2 materials, confirming the nitrogen incorporation into TiO2 P25 [35].

The morphological structure of pure TiO2 P25 and N-doped TiO2 was assessed to determine whether the particle size changed with nitrogen doping using SEM and HR-TEM (Figure 2). There was no particular particle size change on nitrogen doping until TC50 compared to TiO2 P25, where the spherical nanoparticles were observed (Figure 2a–e). Though the change of particle size was not clearly observable from SEM images, the surface area was investigated by an N$_2$ adsorption desorption isotherm (Figure S2). The BET surface area and the pore volume for pure TiO2 P25 and synthesized N-doped TiO2 materials are given in Table S1. From N$_2$ adsorption desorption isotherm it is clearly seen that the surface area decreased with nitrogen doping, suggesting the doping of nitrogen into TiO2. Figure 2f depicts the HR-TEM image of TC10. The lattice fringe with d-spacing of 0.350 nm and 0.240 nm was observed due to the anatase (101) lattice planes of TiO2 nanoparticles and 0.320 nm due to the rutile (110) lattice plane of pure TiO2 P25 [36].
XPS was carried out to investigate the surface chemical composition and the electronic state of each element. The XPS survey scan spectra and elemental composition of pure TiO$_2$ P25, TC10, and TC50 are provided in Supporting Information Figure S1 and Table S2. The photoelectron peaks on the survey spectra at around the binding energies of 285, 399, 459.5, and 530.5 eV were assigned to C1s, N1s, Ti2p, and O1s, respectively, indicating the presence of nitrogen in the N-doped TiO$_2$ materials. Here, the nitrogen contents increased with increasing TCA contents in Table S2, suggesting incorporating nitrogen into TiO$_2$ lattice. The N1s spectrum in Figure 3a consists of three peaks at 399.6, 397.3, and 395.8 eV. The peak at around 399.6 eV is characterized by the absorbed NH$_x$ at the surface of the particle. The peak at 397.3 eV is assigned to Ti-O-N bond; it is due to the interstitial position of N into TiO$_2$ lattice. Furthermore, around 395.8 eV peaks are attributed to the Ti-N-Ti bond due to N substitutional doping on the oxygen site into the TiO$_2$ lattice [39]. Figure 3b shows the O1s spectra of pure TiO$_2$ P25, TC10, and TC50. The peak at 529.4 eV is marked for the Ti-O bond [38]. The minor peak at 531.3 eV is possibly characterized by the impurity hydrocarbon C=O bond [39]. The substitutional Ti-N-Ti bond was also confirmed from the Ti2p XPS spectrum. Figure 3c illustrates the Ti2p spectra of pure TiO$_2$ P25 compared to as-prepared samples of TC10 and TC50. For pure TiO$_2$ P25, at 463.9 eV and 458.3 eV the peak positions confirm the Ti2p$_{1/2}$ and Ti2p$_{3/2}$, which affirms the presence of Ti in the Ti$^{4+}$ species [33]. At 463.6 eV and 458.2 eV, minor peaks in N-doped TiO$_2$ are mainly due to Ti2p$_{1/2}$ and Ti2p$_{3/2}$ of Ti$_2$O$_3$, which are usually found due to oxygen vacancy creation on the lattice structure [39]. In comparison to pure TiO$_2$ P25, the N-doped TiO$_2$ had a shift of binding energy to higher energy for both O1s and Ti2p peaks due to the interaction between titanium and nitrogen [40].
Photoluminescence (PL) analysis of pure TiO$_2$ P25 and the prepared N-doped TiO$_2$ for different nitrogen contents was performed at an excitation wavelength (266 nm) to investigate the rate of recombination and separation efficiency of photo-excited electrons and hole pairs. The PL intensity mainly resulted from the recombination of e$^-$/h$^+$ pairs. The lower intensity suggests a lower recombination rate and higher separation efficiency of e$^-$/h$^+$ pairs [41]. Figure 4a demonstrates the PL spectra of pure TiO$_2$ P25 and the synthesized N-doped TiO$_2$. The PL peaks were found at around 522 nm for pure TiO$_2$ P25, possibly due to the partially reduced titanium ion, surface nitrogen species, and oxygen vacancies [42]. In pure TiO$_2$, usually the energy levels of oxygen vacancies are below the CB of TiO$_2$. The photogenerated electrons in the CB of TiO$_2$ can fall into the oxygen vacancies by the non-irradiation process and then are easily recombined with photogenerated holes on the VB generated by fluorescence emissions [43]. In this study, the PL intensity of N-doped TiO$_2$ decreased and, thus, increased the separation efficiency of photogenerated e$^-$/h$^+$ pairs due to capturing of the photogenerated holes by reduced titanium ion (Ti$^{3+}$). UV–Vis DRS spectroscopy analysis was performed to determine the estimated energy bandgap of pure TiO$_2$ P25 and synthesized N-doped TiO$_2$ materials. Figure 4b illustrates the absorbance spectra of TiO$_2$ and N-doped TiO$_2$ for different nitrogen contents. In this study, the N-doped TiO$_2$ materials compared to pure TiO$_2$ showed yellow color (Figure 2b), suggesting the ability to absorb light in the visible region [40]. The N-doped TiO$_2$ with increasing nitrogen content exhibited a significant red-shift of the absorption edge into the visible light region. This result suggests that nitrogen doping into the TiO$_2$ lattice can successfully narrow the bandgap energy due to modifying the band structure [44].

![Image of PL spectra and UV–Vis DRS spectra](image)

Figure 4. (a) PL spectra and (b) UV–Vis DRS spectra of pure TiO$_2$ P25 and synthesized materials.

The energy bandgaps of the pure TiO$_2$ P25 and synthesized N-doped TiO$_2$ materials with different nitrogen contents were determined using the Kubelka–Munk function (F(R)). Extrapolating (F(R)hυ$^{1/2}$ vs. hυ plot is used to calculate the indirect semiconductor energy bandgap. The estimated energy band gaps were 3.25, 3.22, 3.18, 3.14, and 3.10 eV for pure TiO$_2$ P25, TC7.5, TC10, TC25, and TC50, respectively (Figure 5a). The estimated energy bandgap also revealed the substitutional doping of nitrogen into the TiO$_2$ lattice since interstitial nitrogen doping narrows the energy bandgap significantly more than substitutional doping does [45]. Figure 5b demonstrates the Mott–Schottky plot of pure TiO$_2$ P25 and N-doped TiO$_2$ with different nitrogen contents at 495.16 Hz. In this study, the flat-band potential (Efb) was determined by the Mott–Schottky plot as conduction band minimum (CBM), and the valence band maximum (VBM) was estimated based on the difference from the CBM using the “optical bandgap energy” determined by the Tauc plot. The Schottky formula can be applied to measure the flat-band potentials and the conduction band edge of pure TiO$_2$ and N-doped TiO$_2$, since thin compact TiO$_2$ film behaves similarly to conventional macroscopic semiconductor electrode [46]. TiO$_2$ is an n-type semiconductor,
where vacancies act as electron donors. In Mott–Schottky measurements, a semiconductor is in contact with a solution where a redox couple is present. An electron exchange can then occur to match the two Fermi energies (E_f and E_redox). Such electron flow induces a band bending. The flat band potential (E_B) is a counter-potential that flattens the potential back again by compensating the migrated charge capacity effects, which is measured from the M-S plot. Here, the measured flat band potential represents the lower edge of the conduction band, which is approximately the Fermi energy value, on an electrochemical scale [47]. The figure shows that the increase in nitrogen content resulted in a steady shift of the estimated flat-band potentials towards more negative values. The calculated CB and VB potential values are given in Table S3, and the synthesized sample energy diagrams are given in Figure 6a. The potentials were recalculated vs. NHE at pH 7 by the following equations [46].

\[
V_{CB} \approx V_{FB(NHE, \text{pH } 7)} = V_{FB(Ag/AgCl, \text{pH } 5.8)} + V - 0.059 \times (7 - 5.8) \\
V_{VB} = V_{CB} + E_g/e
\]

(1)

Figure 5. (a) Tauc plot and (b) Mott-Schottky plot of pure TiO_2 P25 and synthesized materials.

Figure 6. (a) Energy diagram with an energy bandgap, CB and VB edge potentials of pure TiO_2 P25 and N-doped TiO_2 materials, and (b) schematic for NO oxidation mechanism of TiO_2 under light irradiation.
The N-doped TiO₂ with different nitrogen contents showed the steady shift of CB and VB potentials towards more negative and less positive directions (Figure 6a). The nitrogen incorporation into TiO₂ lattice had the advantage to form new energy states since the N 2p position is more negative than the O 2p state, which thus decreases the energy bandgap of TiO₂ and shifts the optical absorption towards the visible light region. Therefore, under visible light irradiation, the possibility of electron migration from the valence band to the conduction band increased, which leads to the activity of N-doped TiO₂ materials into visible light [45,48].

A proposed schematic for the oxidation of NO is depicted in Figure 6b. The TiO₂ incited under photo irradiation and generated e⁻/h⁺ pairs. The photogenerated e⁻ can immediately reduce adsorbed O₂ to O₂⁻ on CB, and the h⁺ can directly oxidize H₂O/OH⁻ to OH radicals on VB. Such O₂⁻ and OH radicals are the fundamental elements for the successful oxidation of NO to neutral component NO₃⁻ [49]. The more negative the CB band potential is (than the O₂/O₂⁻ potential of −0.33 eV) and the more positive the VB band potential is (than OH⁻/OH potential of 1.99 eV), the greater the oxidation of NO [33]. The reactions correspond to the formation of radicals, and a feasible pathway for NO oxidation is as follows [49]:

\[
\text{photocatalyst} + h\nu \rightarrow e^- + h^+
\]  
\[
O_2 + e^- \rightarrow O_2^-
\]  
\[
OH^- + h^+ \rightarrow OH
\]  
\[
NO + O_2^- \rightarrow NO_3
\]  
\[
NO + OH \rightarrow NO_2
\]  
\[
NO_2 + OH \rightarrow NO_3^-
\]

Figure 7 demonstrates the time profile for NO, NO₂, and NO₃ and the efficiency of NO removal, NO₂ generation, NO₃ removal, and NO₃⁻ selectivity of pure TiO₂ P25 and the synthesized N-doped TiO₂ sample under both UV and visible light irradiation, respectively, for 1h. All samples compared to pure TiO₂ P25 exhibited enhanced NO oxidation. Under UV irradiation (Figure 7a, Table S4), the TC10 sample exhibited the maximum NO removal with a superior efficiency of 59% compared to the pure TiO₂ P25 (47%), approximately 1.26 times higher. The NO₃ removal efficiency of the TC10 (34%) was increased by 17% compared to TiO₂ P25 (17%) under UV irradiation. The intensified NO expulsion could be clarified by the fact the narrow energy bandgap with more negative CB potentials facilitates the reduction of O₂ to O₂⁻ radicals and, thus, intensifies the formation of the photo-oxidation product (i.e., NO₃⁻). It is further validated by the decreasing trend of the NO₂ generation rate. Here, NO₂ generation was decreased (Figure 7c) over TC10 compared to TiO₂, which leads to higher NO₃ removal.

Under visible light irradiation (Figure 7b, Table S5), all the synthesized N-doped TiO₂ materials exhibited significantly enhanced photocatalytic performance in both NO and NO₃ removal compared to pure TiO₂ P25 samples, though the NO₂ generation is relatively higher than pure TiO₂. Among all the samples, TC10 showed maximum NO and NO₃ removals of 51% and 29%, respectively, almost 2.55 and 2.23 times higher than the pure TiO₂ P25 of 20% and 13%. Nitrogen doping into the TiO₂ lattice enhanced the absorption ability towards the visible light region and narrowed the energy bandgap with more negative CB potentials, which enhanced the formation of superoxide radicals and, therefore, oxidation of NO. For practical application, the goal is to produce materials with high selectivity to NO₃⁻. Comparing Tables S4 and S5, the selectivity of NO₃⁻ of pure TiO₂ significantly differed and was much higher under visible irradiation (about 64%). This phenomenon can be explained by the energy band structure of pure TiO₂ and N-doped TiO₂. As we mentioned, the more negative the CB band potential than the O₂/O₂⁻ potential (−0.33 eV), and the more positive the VB band potential than OH⁻/OH potential (1.99 eV), the greater
the oxidation of NO and the formation of NO$_3^-$.

For pure TiO$_2$ the more positive valence band (2.59 eV vs. NHE) than doped TiO$_2$ (<2.53 eV vs. NHE) favors NO$_3^-$ formation on the valence band (favors Equation (7)). However, in case of VIS experiment of TC50, a superior increase in NO$_3^-$ selectivity was shown (77%). This might be due to the direct conversion of NO to NO$_3^-$ on the more negative conduction band (−0.84 eV vs. NHE) than pure TiO$_2$ (−0.66 eV vs. NHE), which is more favorable for reduction of NO and formation of NO$_3^-$ (favors Equation (5)). Compared to pure TiO$_2$ P25, for the N-doped TiO$_2$ sample, the generation of NO$_2$ was higher (Figure 7d). This can be explained by the fact that the N-doped TiO$_2$ showed increased charge transfer/separation efficiency. Therefore, the formation of OH radicals on the valence band, followed by formation of NO$_2$, was increased under visible light irradiation. The substitutional nitrogen doping into the TiO$_2$ lattice can enhance the photocatalytic activity of NO oxidation by enhancing its absorption ability towards the visible light region, improving separation efficiency of e$^-$ /h$^+$ pairs, and narrowing the energy band gaps under both UV and visible light irradiation.

Here, NO$_x$ removal performance was compared with some other progressive studies (Figure 8). Nitrogen-doped with P25 using urea as a precursor achieved NO$_x$ removal performances of approximately 18% and 8% at UV and visible regions, respectively [19,50–52]. Composite of carbon nitride with anatase TiO$_2$, composite of modified carbon nitride with TiO$_2$, and composite of hydroxyapatite with TiO$_2$ achieved 18/17, 24/18, and 27/0% NO$_x$ removal proficiencies in the UV/visible region, respectively [19,50–52]. In the present study, 34/28% NO$_x$ removal was attained in the UV/visible region, which indicates significant progress for the NO$_x$ removal strategy. The present study can be further improved by making a composite with carbon nitride with advanced synthesized N-doped TiO$_2$ in the future.
27/0% NOx removal proficiencies in the UV/visible region, respectively [19,50–52]. In the present study, 34/28% NOx removal was attained in the UV/visible region, which indicates significant progress for the NOx removal strategy. The present study can be further improved by making a composite with carbon nitride with advanced synthesized N-doped TiO2.

3. Materials and Methods

3.1. Preparation of N-Doped TiO2

All the chemicals were used as of analytical grade without further purifications. The N-doped TiO2 powder was synthesized as follows. Firstly, tri-thiocyanuric acid (TCA, Sigma-Aldrich, St. Louis, MO, USA; 95.0%) was dissolved into 10 mL dimethyl sulfoxide (DMSO, Daejung, Siheung, Korea, 99.5%), and TiO2 P25 (Evonik Degussa GmbH, Essen, Germany) was dispersed into 20 mL of H2O by sonication for 1h. Then, the solution was mixed and kept for 1 h followed by filtering and drying at 80 °C. The dried powders were then calcined in a tube furnace at 550 °C for 4h under an N2 atmosphere. Different TCAs (50, 25, 10, and 7.5 wt.%) were mixed with TiO2 P25 and named as TC50, TC25, TC10, and TC7.5, sequentially, to prepare the N-doped TiO2 powder. The pure TiO2 P25 was named TiO2.

3.2. Characterization

The crystallinity of synthesized powders was evaluated using the X-ray diffraction (XRD) technique (Rigaku D/max Ultima III, The Woodlands, TX, USA) with Cu Kα radiation at 40 kV and 40 mA. The synthesized powder surface morphology was assessed using scanning electron microscopy (FE-SEM, HITACHI, EX-200, Santa Clara, CA, USA). High-resolution transmission electron microscopy (HR-TEM, TECNAI F20 UT) was used to examine the N-doped TiO2 morphology’s fine details. A Fourier transform infrared (FT-IR) spectrometer (FT-IR-4100, Jasco, Portland, OR, USA) equipped with an integrating sphere accessory was used to obtain the synthesized sample UV–vis spectra.
samples. The indirect energy bandgap was verified by extrapolation of \((F(R)h\nu)^{1/2}\) vs. \(\nu\) plot. The specific surface area was measured by \(N_2\) adsorption–desorption measurements at 77 K (Micromeritics new Tristar II surface area and porosity analyzer 3020, USA) using the Branauer–Emmet Teller (BET) method. The samples were degassed at 150 °C for 24 h before measurements.

3.3. Electrochemical Measurements

The electrochemical performance of the synthesized N-doped TiO\(_2\) was examined using Bio-logic VSP potentiostat equipped with a handmade three-electrode cell containing conductive fluorine-doped tin oxide (FTO) as a working electrode, Pt electrode as a counter, and Ag/AgCl KCl (3 M) electrode as a reference electrode, respectively. The electrode materials were prepared by dispersing 50 mg of investigated materials in 2 mL solution containing 1.8 mL of ethanol (DAEJUNG) and 0.2 mL of Nafion (Sigma Aldrich, St. Louis, MO, USA 5 wt% in ethanol), followed by sonication and stirring. After that, 100 µL of the dispersion was cast on the FTO electrode, followed by drying at 60 °C for 8 h. The electrolyte used in the experiment was 0.2 M sodium sulfate (Na\(_2\)SO\(_4\), Sigma Aldrich, 99%, Darmstadt, Germany). Before measurements, \(N_2\) gas was purged for 30 min. The experiment was performed at room temperature. These measurements were performed to calculate the CB edge potential of synthesized samples. While the CB edge potentials and flat band potentials practically coincide for n-type semiconductors, the Mott–Schottky relation can be used for the determination of \(V_{FB}\) [46].

\[
\frac{1}{C^2} = \frac{1}{\varepsilon\varepsilon_0N_D} (V - V_{FB} - \frac{kT}{e})
\]  

(8)

Here, \(C\) is the space charge capacitance, \(\varepsilon\) and \(\varepsilon_0\) are the dielectric constants of the semiconductor and free space, \(e\) is the charge of the elementary electron, \(N_D\) is the dopant density, \(k\) is the Boltzmann constant, and \(T\) is the absolute temperature. The flat band potential \(V_{FB}\) is determined by intercepting the plot’s linear part with the potential axis.

3.4. Photocatalytic Activity Measurements

The NO\(_x\) removal efficiencies of pure TiO\(_2\) P25 and the synthesized N-doped TiO\(_2\) samples were determined using a NO\(_x\) removal photocatalytic analyzer (KS ISO 22197-1 standard) under both UV and visible light irradiation. The emission spectra of UV and visible light sources are given in Figure S3 in the Supporting Information. According to ISO protocol, the reaction parameters were maintained at 1 ± 0.003 ppm initial NO concentration, 3 L/min gas flow, relative humidity of 50%, and reaction temperature of 25 °C. The samples were prepared by casting a slurry of catalyst powders and water on a glass plate, and the exposed catalyst surface had an area of 40 cm\(^2\). The loading mass for each sample was 5 mg cm\(^{-2}\). During the measurement procedure, the UV and visible light intensities were 1.00 ± 0.30 W m\(^{-2}\) and 6000 ± 300 lux. All the experiments were performed for 100 min, where 20 min was used for adsorption of gas and 60 min for light irradiation. To measure the NO and NO\(_2\) concentrations, a NO\(_x\) analyzer (Sernius 40, Ecotech, Melbourne, Australia) was fixed at the reactor’s outlet. The rates of NO removal, NO\(_2\) generation, NO\(_x\) removal, and nitrate (NO\(_3^-\)) selectivity were calculated by the following equations:

\[
\text{NO removal} = \frac{\text{NO}_{\text{in}} - \text{NO}_{\text{out}}}{\text{NO}_{\text{in}}}
\]  

(9)

\[
\text{NO}_2\text{ generation} = \frac{\text{NO}_2, \text{out} - \text{NO}_2, \text{in}}{\text{NO}_{\text{in}}}
\]  

(10)

\[
\text{NO}_x\text{ removal} = \frac{\text{NO}_{x, \text{in}} - \text{NO}_{x, \text{out}}}{\text{NO}_{\text{in}}}
\]  

(11)

\[
\text{NO}_3^-\text{ selectivity} = \frac{\text{NO}_3^-\text{ removal}}{\text{NO}_{\text{removal}}} \times 100
\]  

(12)
4. Conclusions

In the present study, nitrogen-doped TiO$_2$ was prepared in a straightforward way by calcination of precipitates from the solution mixture of tri-thiocyanuric acid in DMSO and TiO$_2$ P25 in H$_2$O. The optimized TC10 materials showed impressive light absorption capability in the visible region by narrowing the bandgap (TC10: 3.18 eV; TiO$_2$ P25: 3.25 eV). The ratio of nitrogen doping assisted in tuning the conduction band and valance band positions. Most significant, the electron and hole separation efficiencies were improved for nitrogen doping on the titanium oxide. Consequently, the TC10 (N doped TiO$_2$ P25) removed 51% NO and 28% NO$_x$, which are 2.55 and 2.23 times higher than that for pure TiO$_2$ P25 in the visible region. Similarly, in the UV region, TC10 removed 59% NO and 34% NO$_x$, which was 2.62 and 2 times higher than that for TiO$_2$ P25. N-doped titanium oxide (TC10) is a unique material that offers excellent potential to remove noxious nitrogen oxide (NO$_x$) from the environment and maintain sustainable urban life for the well-being of human continued existence.

Supplementary Materials: The following are available online at https://www.mdpi.com/2073-4344/11/1/109/s1, Figure S1: The broad scan survey spectra of pure TiO$_2$ P25 and N-doped TiO$_2$ samples with 10 wt% and 50 wt% nitrogen contents. Figure S2: N$_2$ adsorption desorption isotherm of pure TiO$_2$ P25 and synthesized N-doped TiO$_2$. Figure S3: Emission spectra of (a) UV, and (b) visible light sources. Table S1: Estimated FWHM and crystal size of the prepared samples along with the anatase (101) plane of TiO$_2$, and BET surface area and pore volume from N$_2$ adsorption desorption isotherm. Table S2: XPS elemental analysis of purer TiO$_2$ P25 and N-doped TiO$_2$ samples with 10wt% and 50wt% nitrogen contents. Table S3: The energy band gap, CB and VB edge potential of pure TiO$_2$ P25 and N-doped TiO$_2$ samples. The CB and VB edge potentials was measured vs Ag/AgCl at pH 5.8 and calculated vs NHE at pH 7. Table S4: Photocatalytic efficiency of samples in NO removal, NO$_2$ generation, NO$_x$ removal and NO$_3^-$ selectivity under UV irradiation. Table S5: Photocatalytic efficiency of samples in NO removal, NO$_2$ generation, NO$_x$ removal and NO$_3^-$ selectivity under visible light irradiation.


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References


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