Effect of Urea Addition on Anatase Phase Enrichment and Nitrogen Doping of TiO₂ for Photocatalytic Abatement of Methylene Blue

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Abstract: TiO₂-based materials are commonly employed as photocatalysts for industrial wastewater treatment. The primary reasons of employing TiO₂ include cost effectiveness, ready availability, eco-friendliness, non-toxic behavior, and exceptional resistance towards photo-corrosion. However, the wider band gap of pure TiO₂ restricts its performance because of its optical absorption of solar light to the ultraviolet (UV) region only, and to some extent of photo-excited charge recombination. In the present work an attempt is made to develop a facile synthesis approach by using urea, a cheap chemical precursor, to form nitrogen doped TiO₂ with the key objective of extended light absorption and thus enhanced photocatalytic performance. It was also observed that the urea-induced anatase phase enrichment of TiO₂ is another key factor in promoting the photocatalytic performance. The photocatalysts prepared by varying the amount of urea as a nitrogen dopant precursor, are characterized using X-ray diffraction (XRD), scanning electron microscopy (SEM), Fourier transform infrared (FTIR) spectroscopy, and photoluminescence (PL) to evaluate their crystallinity, morphology, functional groups, and charge separation properties, respectively. Moreover, the surface area was also estimated by physicochemical adsorption. The maximum nitrogen-doped sample yielded >99% photodegradation efficiency of methylene blue (MB) dye-simulated wastewater as compared to a pure TiO₂ sample which exhibited 6.46% efficiency. The results show that the simultaneous factors of nitrogen doping and anatase phase enhancement contributes significantly towards the improvement of photocatalytic performance.

Keywords: photocatalysis; nitrogen doping; anatase phase enrichment; textile wastewater treatment

1. Introduction

The industrial contamination of water, soil, or air, has always been an alarming issue for the human beings and life on Earth [1–4]. One vital constituent that severely affects the earth lifecycle is use of unhygienic and contaminated water due to industrial effluents and pollution. Hence, surrounded by industrialization and farming leftover, the major cause of organic impurities in water can be ascribed to the disposal of industrial wastewater without proper treatment. Amongst industries, the textile industry contributes to a great extent to
water contamination and pollution, specifically in developing or underdeveloped countries [3,5,6]. The toxins present in textile wastewater consist of unmanageable toxic-colored dyes, surfactants, along with many chlorine-containing amalgams [3,5,7]. These dyes have the ability to persist in the environment for a prolonged time. The textile industry employs a variety of dyes which mainly consists of azo compounds, anthraquinones, diarylmethanes, phthalocyanines, etc. As reported approximately 70% of industrial wastewater consists of azo dyes [7]. These azo dyes are cancer-causing and also mutagenic in nature. They come into the body through incorporation as well as processing via gastric microbes and harming human and animal life.

Recent investigations have paid attention to numerous wastewater treatment procedures such as biodegradation, coagulation, adsorption, chemical treatment, advanced oxidation processes (AOPs), and membrane processes [8]. Amongst the abovementioned approaches, AOP seems one of the favorable methods for degradation of organic dyes as it is a cost-effective, easy, and competent approach with the ability to degrade dye compounds into CO$_2$, water and other less hazardous intermediates. Amongst the various AOPs, photocatalysis is considered as a viable, renewable and eco-friendly approach for wastewater treatment [9–12]. Photocatalysis employs a photocatalyst, generally a semiconductor material, and light for the treatment of organic compounds in wastewater. Under light irradiation, photo-excited charges are generated which initiate electrochemical reactions with wastewater on their surface and decompose the organic contaminants completely or partially into harmless intermediates. Amongst the variety of photocatalysts being investigated, titanium dioxide (TiO$_2$) is still a widely used photocatalyst because of its abundance, cost effectiveness and excellent properties such as nontoxicity, high excitation binding energy, and photocatalytic active crystal phases (anatase, rutile and brookite) [13–16]. Despite of all these benefits, TiO$_2$ has some major drawbacks including its limited optical absorption, i.e., limited light absorption due to a wide band gap (3.2 eV), and moderate recombination of photo-excited charge carriers (e$^-$/h$^+$), influencing its photocatalytic performance. Hence, to improve the photocatalytic performance of TiO$_2$, several strategies have been employed with the objective of narrowing down the band gap of TiO$_2$ which include methods such as metal and non-metals doping [17], noble metal loading [18,19], hetero-junction structures [16,20–24] and TiO$_2$-based composites [20,23,25,26]. Doping/co-doping with non-metals e.g., nitrogen, sulphur, carbon, fluorine, etc. in TiO$_2$ framework, are economical and capable of narrowing down the band gap leading to efficient photocatalyst behavior due to the resulting enhanced optical absorption [27,28].

Amongst the various doped TiO$_2$ materials, nitrogen-doped TiO$_2$ (N-TiO$_2$) have received wider attention for various applications. In N-TiO$_2$, nitrogen impurities are incorporated into the TiO$_2$ lattice, influencing mainly the optical properties via generation of new states leading to enhanced photocatalytic performance [29,30]. Until today a variety of procedures have been adopted for the synthesis of N-TiO$_2$ such as gas annealing processes (using gases such as ammonia), or by a wet chemical approaches employing thiourea, liquid ammonia, hydrazine or nitric acid as a nitrogen doping source [29–40]. Although all such approaches provide efficient photocatalysts with improved performance, however they utilize somewhat complex procedures for the nitrogen doping during the synthesis process. Hence, to overcome the key issue of complex synthesis procedure, and use of risky and unsafe doping precursors such as acids and highly basic ammonia, it is important to develop a synthesis approach which is facile, less complicated and employs no or less toxic doping precursors.

In the present study, a facile two-step synthesis strategy has been proposed, employing urea as an inexpensive nitrogen source for nitrogen doping, which can lower the cost of doped TiO$_2$ for textile wastewater treatment. Urea interestingly also intensifies the anatase phase of TiO$_2$ when its amount is increased. As well-established, TiO$_2$ anatase phase is the most photocatalytic-active phase, thus the synergistic effect of urea as a dopant source leads to the formation of narrowed band gap nitrogen-doped TiO$_2$ with an enriched anatase
phase. The photocatalytic performance of the prepared samples was evaluated by their tendency to degrade a simulated MB dye-containing wastewater.

2. Materials and Methods

2.1. Chemicals and Materials

The materials and reagents employed for the synthesis of the photocatalyst includes: Titanium (IV) isopropoxide (TTIP, 97%, Sigma Aldrich, Beijing, China), ethanol (C₂H₅OH, 96%, Sigma Aldrich), urea ((CH₄N₂O), 98%, Daejung Chemicals, Daejeon, South Korea) were used. Deionized (DI) water having resistivity > 18.0 MΩ and conductivity of 0.055 µS was used for washing purposes during all the experiments. Methylene blue (MB, Sigma Aldrich, Bangalore, India) dye was purchased and employed to evaluate the photocatalytic activity of the prepared samples.

2.2. Synthesis of Pure and Nitrogen-Doped TiO₂ Samples

The synthesis of nitrogen-doped TiO₂ (NT) was accomplished by a facile two step synthesis strategy. In the first step a specified amount of urea is completely dissolved in ethanol (50 mL) followed by addition of a fixed volume (4.6 mL) of TTIP. Upon addition of TTIP, white precipitates of Ti(OH)₂ are formed rapidly which are kept under stirring for at least 1 h to achieve homogeneous mixing. In the second step, this solution containing Ti(OH)₂ precipitates is evaporated by placing the solution on a hotplate until a white powder is left over. The obtained samples were washed with DI water, dried at 100 °C in an oven for 24 h followed by calcination at 450 °C for 5 h in a muffle furnace resulting in yellow colored NT samples. To study the influence of urea as a doping precursor, three different samples were prepared with varied amounts of urea i.e., 0.983 g, 1.965 g and 2.940 g, identified as NT-1, NT-2, and NT-3, respectively. As a reference pure TiO₂ was also synthesized by following the same procedure.

2.3. Materials Characterizations

The crystallinity of the as-prepared photocatalysts were examined by X-ray diffraction (XRD), using an X-pert powder diffractometer (PanAnalytical, Almelo, Netherlands) furnished with Cu-Kα (X-ray wavelength of 1.5406 Å), within 2θ = 10–80° range, scan-speed of 200 seconds/step and a step-size of 0.02°. Morphological analysis of the samples was performed by using scanning electron microscopy (SEM, TESCAN Vega LMU, Tescan, Kohoutvoice, Czech Republic) operating at 15 kV voltage. The size estimation of the nanoparticles employing SEM images was performed using the Image J 1.53 K software. Raman and photoluminescence (PL) spectra were obtained using an InVia Raman microscope (Renishaw, Wotton-under-Edge, England, UK) with a 514 nm excitation laser light source. Fourier transform infrared (FTIR) spectra were recorded for functional group analysis using a Spectrum II spectrometer by Perkin Elmer (Waltham, MA, USA) in the attenuated total reflectance (ATR) mode. Thermogravimetric analysis (TGA) of the samples were performed using a TGA-701 instrument (LECO, St. Joseph, MI, USA). Thermogravimetric analysis (TGA) of all samples was performed under continuous air flow (60 mL/min), heating up to 500 °C with a ramp of 20 °C/min.

UV-Vis diffuse reflectance spectra (DRS) of the samples were recorded using a V-770, UV-Visible/NIR spectrophotometer (Jasco, Mary’s court, Easton, PA, USA) within a wavelength range of 200–800 nm. Surface area of the as prepared samples was examined using a Tristar II 3020 system (Micrometrics, Norcross, GA, USA). All the samples were degassed at 150 °C, before analysis, and the isotherms were controlled at −196 °C. The exposed surface area of the samples was examined using Brunauer-Emmet-Teller (BET) method. The BET equation employed for surface area measurement of the samples is as follows [41]:

$$ S = X_m L_{av} A_m / M_v $$

where $S$ = Total surface area. $X_m$ = Monolayer capacity. $L_{av}$ = Avogadro’s number. $A_m$ = cross sectional area of the adsorbate. $M_v$ = Molar volume of the gas absorbed.
The electronic states of Ti, O, N and C in pure TiO$_2$ and NT-3 samples were analyzed by X-ray photoelectron spectroscopy (XPS) using Al Kα line as X-ray source. Peaks fitting for the XPS spectrum was done by the Gaussian method.

2.4. Photocatalytic Performance Evaluation

The photocatalytic activity performance of the as-prepared materials was assessed by the photocatalytic degradation capability for MB dye simulated textile wastewater. In brief 0.05 g of the photocatalyst was added to 100 mL of a 5.0 mgL$^{-1}$ aqueous solution of MB dye and photocatalytic degradation efficiency was investigated. The solution was stirred for 60 min. in dark to achieve adsorption-desorption equilibrium between the photocatalyst and the dye. Afterwards the MB dye solution with photocatalysts is subjected to light illumination generated by 500 W xenon lamp for 120 min. An aliquot of 5.0 mL of the solution was recovered from the solution every 30 min., during the illumination period, centrifuged (6000 rpm for 5 min, Pro Research K241, Centurion Scientific, Chichester, UK), and MB dye degradation analyzed using UV-Vis absorption spectrometer (Biobase, BK-UV1900 PC, Jinan, China).

The formula for calculating the photocatalytic efficiency (%) is presented in Equation (2):

$$\text{Photocatalytic efficiency (\%)} = \left( \frac{(C_0 - C_t)}{C_0} \right) \times 100$$

where, $C_0$ (mg L$^{-1}$) is the initial concentration and $C_t$ (mg L$^{-1}$) is the concentration at time $t$, after light irradiation.

3. Results and Discussion

3.1. Crystallinity

The crystallinity of the prepared samples was investigated by obtaining the corresponding XRD patterns, as exhibited in Figure 1. It is obvious that all samples display diffraction peaks occurring at 2θ values of 25.2, 37.9, 48.1, 62.8 and 75.16 degrees, corresponding to $d_{101}$, $d_{004}$, $d_{200}$, $d_{204}$ and $d_{215}$ of anatase phase, [16,42] with no additional peak or peak shifting being observed upon urea addition. However, few peaks of rutile phase with low intensity are also observed appearing at 2θ values of 54.64, 56.56, 69.26, 69.83 degrees corresponding to $d_{211}$, $d_{220}$, $d_{301}$, $d_{112}$ of rutile phase, respectively [43,44]. Furthermore, all the peaks of anatase phase are increased with the increment of the urea amount. Such an effect can be explained based on the pH increment that occurs with the addition of the urea in solution, promoting the formation of anatase phase. When urea is dissolved in ethanol solvent, the pH value of the solution increases. Further on addition of TTIP, the urea can react with H$_2$O to produce ammonium hydroxide (NH$_4$OH), carbon dioxide and ammonia gas [45]. The ammonium hydroxide can be dissociated to NH$_4^+$ and OH$^-$ to hydrolyze Ti$^{4+}$, and the presence of ammonia increases the pH of solution, which finally results in higher anatase phase composition. Thus, urea simultaneously promotes the formation of anatase phase as well as nitrogen doping of TiO$_2$.

Further investigation of the crystalline phase and Raman modes of vibration were analyzed using Raman spectroscopy as shown in Figure 2. It can be observed that all samples exhibit Raman bands at 148 cm$^{-1}$, 400 cm$^{-1}$, 515 cm$^{-1}$ and 640 cm$^{-1}$ which mainly corresponds to anatase TiO$_2$ [16,46]. The intensity of all the mentioned peaks intensifies with the increase of urea concentration as it goes from pure TiO$_2$ to NT-3 sample, thus confirming the urea effect for anatase phase enrichment. Moreover, the increased intensity of all the Raman peaks can be ascribed to the enhanced crystallinity along with enriched anatase phase.
Figure 1. XRD patterns of pure TiO$_2$, NT-1, NT-2 and NT-3, synthesized by using 0.0 g, 0.983 g, 1.965 g and 2.940 g of urea respectively (A: anatase phase, and R: rutile phase).

Figure 2. Raman spectra of pure TiO$_2$, NT-1, NT-2 and NT-3, synthesized by using 0.0 g, 0.983 g, 1.965 g and 2.940 g of urea respectively.

3.2. Morphological Analysis

The morphological analysis of as-prepared samples was carried out by performing scanning electron microscopy, as shown in Figure 3. Spherical aggregated morphology with a high packing density and narrow particle size distribution can be seen for all synthesized samples. However, the diffusion of nanospherical aggregates was observed at multiple locations owing to the addition of nitrogen into the titania lattice. It is further observed that the addition of urea reduces the agglomeration of nanoparticles, with the increased size of nanoparticles. On further increasing the amount of urea, the nanoparticles dispersion deteriorates, and agglomeration again dominates but the size of nanoparticles becomes smaller, revealing a narrower particle size distribution. The average sizes of the nanoparticles estimated using SEM images (via Image J software) are found as: 146 nm for pure TiO$_2$, 116 nm for NT-1, 115 nm for NT-2, and 109 nm for NT-3 samples.
3.3. Fourier Transform Infrared Spectroscopy (FTIR) Analysis

The doping of nitrogen into the titania lattice was further confirmed by the FTIR spectra. The FTIR spectra of all as-prepared samples are shown in Figure 4. The complete spectrum is shown in Figure 4a, whereas the enlarged view of regions between 750–2000 cm\(^{-1}\), and 2000–4000 cm\(^{-1}\) are shown in Figure 4b,c, respectively. The transmittance peaks for pure TiO\(_2\) can be observed within range of 1100–1200 cm\(^{-1}\) and is associated to the stretching vibrations of Ti-O and Ti-O-Ti bonds in the TiO\(_2\) lattice (Figure 4b). The peaks observed near 1636 cm\(^{-1}\) (Figure 4b) and 3440 cm\(^{-1}\) (Figure 4c) corresponds to the bending and stretching vibrations of the O-H bond related to the absorbed water molecules [47,48]. For all NT samples the transmittance peaks are observed appearing in the ranges of 1000–1100 cm\(^{-1}\) (Figure 4b), and 2800–3000 cm\(^{-1}\) (Figure 4c). The two peaks appearing in the first region at 1040 and 1090 cm\(^{-1}\), can be attributed to the interstitial N-O bond and Ti-O-N bond, respectively [32,49]. However, the peaks observed in the second region are probably due to the presence of C-H stretching vibrations because of organic species from the synthesis precursors during calcination [32].

3.4. Thermogravimetrical Analysis (TGA)

The comparative investigation between pure TiO\(_2\) and NT samples was also supported by thermogravimetric analysis. Figure 5 displays the TGA thermograms for pure TiO\(_2\) and all NT samples. It can be observed that for pure TiO\(_2\) sample, the TGA curve declines in the range of 150–200 °C, indicating a weight loss mainly due to the evaporative loss of water or any organic matter involved during the synthesis. However, the NT samples, on the contrary, exhibits two weight loss regions; the first region in between 150–200 °C and the second region lies between 220–350 °C. The weight loss in the first region can be associated similarly as the evaporative loss of water from pure TiO\(_2\) whereas, the second weight loss region can be attributed to the degradation of an organic matrix such as urea used as nitrogen dopant, as reported earlier [50].
Figure 4. FTIR spectra of pure TiO$_2$, NT-1, NT-2 and NT-3, synthesized by using 0.0 g, 0.983 g, 1.965 g and 2.940 g of urea respectively. (a) The complete spectrum; The enlarged view of regions between 750–2000 cm$^{-1}$ (b), and 2000–4000 cm$^{-1}$ (c).

Figure 5. TGA curves for pure TiO$_2$, NT-1, NT-2 and NT-3, synthesized by using 0.0, 0.983, 1.965 and 2.940 g of urea, respectively.
3.5. Optical Properties Investigation

UV-visible diffuse reflectance spectra (UV Vis DRS) of the prepared samples are shown in Figure 6a. It is obvious that pure TiO$_2$ sample only exhibits light absorbance in the UV region (200–400 nm), with a band appearing around 390 nm. However, upon doping with nitrogen, the NT samples exhibit a clear red shift in light absorption thus supporting the doping of pure TiO$_2$. It is well established that upon doping of external element such as nitrogen, new energy levels are created above the valence band which might results in the extension of light absorption and narrowing of the band gap. The band gap energy ($E_g$) of pure TiO$_2$ and NT samples are also estimated utilizing Tauc’s equation [15,51]. Tauc’s plot is generated by plotting the Kubelka-Munk function ($\alpha h\nu$)$^2$ against band gap energy ($E_g = \frac{h\nu}{\pi}$), where $\alpha$ is absorption coefficient, $h$ is the Plank’s constant, and $\nu$ is the frequency of radiation. The estimation of band gap is then done by extrapolation of the linear portion of curve to the zero value of the $y$-axis. The Tauc’s plots for pure TiO$_2$ and NT samples are shown in Figure 6b. It is noticeable that pure TiO$_2$ possesses a band gap of 3.4 eV, however upon N doping the linear portion of band edge intercepts at $x$-axis value of 2.75 eV, 2.60 eV, and 2.50 eV for NT-1, NT-2 and NT-3 samples, respectively. Hence based on UV Vis DRS measurements and band gap estimation it can be assured that the narrowing down of band gap and extension of light absorption is mainly due to N doping of TiO$_2$ [29–31,34–36,38,40].

Figure 6. (a) UV Vis DRS spectra, and (b) Band gap estimation of, Pure TiO$_2$, NT-1, NT-2 and NT-3.

Figure 7 displays the PL spectra of all as-prepared samples. A sharp peak appearing within the range of 500–530 nm can be attributed to the band to band recombination, whereas a broad hump observed around 600 nm is mainly associated to the defects induced by foreign elements [52,53]. It can be observed that band to band peak is quenched for NT samples as compared to pure TiO$_2$ thus indicating the efficient separation of photo-excited charges, whereas the later broad peak for NT samples is higher as compared to pure TiO$_2$ thus again supporting the recombination of photo-excited charges, trapped by defects which were induced by doping process, and are less on the surface of pure TiO$_2$.

3.6. Surface Area and Porosity Analysis

The surface area of the prepared samples is measured using the BET equation, and is an important parameter contributing the photocatalytic performance. When the surface area is higher the photocatalyst will provide more surface for reactions and thus better performance. The surface area and porosity of as-synthesized samples are summarized in Table 1. The small addition of urea resulted in a minor reduction of the surface area with minimal effect on the pore volume. However, upon increasing the amount of urea, a continual decrease in surface area and pore volume is observed. Thus, it can be seen that the surface area of the NT-3 samples is reduced to approximately 45% of pure TiO$_2$. Such a
decrease in the surface area can be attributed to the agglomeration of TiO$_2$ nanoparticles and increased size as displayed by the SEM images. Thus, nitrogen doping creates defects and narrows the band gap, and with the anatase phase enrichment it makes NT samples more efficient despite their reduced surface area.

![Figure 7. PL spectra of (a) Pure TiO$_2$, (b) NT-1, (c) NT-2 and (d) NT-3.](image)

| Photocatalyst | BET Surface Area [m$^2$/g] | Pore Size [nm] |
|--------------|----------------------------|---------------|
| Pure TiO$_2$ | 42.98                      | 0.6427        |
| NT-1         | 38.87                      | 0.5947        |
| NT-2         | 30.18                      | 0.5788        |
| NT-3         | 23.93                      | 0.5776        |

3.7. X-ray Photoelectron Spectroscopy (XPS)

The surface analysis and oxidation states of the elements in pure TiO$_2$ sample and NT-3 samples are analyzed using XPS. The high resolution XPS spectra with peak fitting for pure TiO$_2$ and NT-3 sample are shown in Figures 8 and 9, respectively. The high resolution XPS of Ti 2p for both samples (Figures 8a and 9a) exhibits the corresponding peaks of Ti 2p$_{3/2}$ and Ti 2p$_{1/2}$ binding energies, indicating the presence of Ti$^{4+}$ ions in both, pure TiO$_2$ and NT-3 the samples [14,15]. Figure 8b displays the high resolution O 1s XPS spectrum with three fitted peaks for pure TiO$_2$ sample, the peaks appearing around 529.18 eV, 531.58 eV and 534.68 eV are attributed to lattice Ti-O bonds [54], and non-lattice O-H and C-O bonds, respectively. The O 1s XPS spectrum for the NT-3 sample (Figure 9b) exhibits similar peaks with a slight shift towards higher binding energy that can be attributed to the effect of N doping. Figure 8c shows N 1s XPS spectrum for pure TiO$_2$ which exhibits only noise rather than any peak and state of N, whereas, for the NT-3 sample, the N 1s XPS spectrum (Figure 9c) clearly displays peaks appearing around the
binding energy of 398.48 eV and 407.48 eV. The former peak is associated to the Ti-N bonds formed after replacement of O atoms with N atoms within the TiO$_2$ lattice [55], whereas the later peak indicates the presence of N atoms chemisorbed on the surface of the NT-3 sample [56]. Figure 8d shows the C 1s XPS spectrum for pure TiO$_2$ samples with the peak fitting showing three peaks. The peak appearing at binding energy of 284.68 eV, is associated to the elemental carbon [57], whereas the peaks appearing at 288.48 eV and 289.88 eV are ascribed to C-O and C=O [58], indicating the presence of carbonaceous species within the samples. The C 1s XPS spectrum for NT-3 sample with peaks fitting is shown in Figure 9d. The peak appearing at 284.98 eV can be attributed to elemental carbon [57], whereas the peaks appearing at 287.78 eV and 289.58 eV can be associated to the C-O and C=O species [58], respectively. In both samples, pure TiO$_2$ and the NT-3 sample, in addition to elemental carbon peaks, the peaks of carbonaceous species can be ascribed to the adsorption of carbon during the synthesis procedure and/or probable formation of Ti-O-C bonds.

Figure 8. High resolution XPS spectra with peak fittings for pure TiO$_2$ sample showing: (a) Ti 2p, (b) O 1s, (c) N 1s, and (d) C 1s, regions.

3.8. Photocatalytic Activity Evaluation

The photocatalytic activity of the prepared photocatalyst samples was evaluated via measuring the photodegradation efficiency of a simulated MB dye wastewater under light irradiation using a xenon lamp as a visible light source, over a period of 120 min (Figure 10). MB dye photodegradation was also tested by using pure TiO$_2$ as a reference sample. It can be seen from Figure 10 that pure TiO$_2$ sample under light irradiation shows negligible MB dye degradation (6.46%), while for NT samples the MB dye degradation performance follows the trend NT-3 > NT-2 > NT-1. Hence the N doping of pure TiO$_2$ by urea addition as well as anatase phase enrichment enhances the photocatalytic performance and increases the photodegradation efficiency from 6.46% for pure TiO$_2$ to greater than 99% for NT-3 samples. Such an enhanced performance can be attributed to the extension of light absorption towards the visible region induced by the energy states created by
nitrogen doping. Such energy states created as a result of doping, narrow down the band gap of the photocatalysts, resulting in generation of increased photo-excited charges under light irradiation. In addition to nitrogen doping, enrichment of the anatase phase with increased urea amount also contributes to the photocatalytic performance. As a control test, photocatalytic dye degradation employing a standard TiO$_2$ nanopowder (Degussa P25) was performed. The dye degradation absorption spectra and relative concentration profile are shown in Figure S2. It can be observed that P25 samples showed better performance (approximately 24% degradation after 120 min.) as compared to the pure TiO$_2$ sample but less efficient than the N-doped TiO$_2$ samples.

Figure 9. High resolution XPS spectra with peak fittings for pure NT-3 sample showing: (a) Ti 2p, (b) O 1s, (c) N 1s, and (d) C 1s, regions.

Figure 10. Photocatalytic degradation of MB dye simulated wastewater by pure TiO$_2$, NT-1, NT-2 and NT-3 samples.
Furthermore, as is well-established, the photodegradation of MB dye is influenced by various parameters, such as nanoparticle size, crystallinity, phase composition, porous nature and surface area. It can be observed that amongst all samples, NT-3 sample exhibited the best performance with the lowest surface area, highest nitrogen doping and highest anatase phase. Such an increased performance might be attributed to these two effects i.e., more anatase phase in the NT samples and increased light absorption due to N doping of TiO$_2$. It is well established that MB dye is considered a basic dye due to presence of cationic groups on its surface such as -NH$_3^+$. The affinity for adsorption for MB dye is enhanced towards anatase TiO$_2$ phase, which is rich in surface OH groups [43,44]. Therefore, when the amount of urea used as a dopant is increased, the anatase phase is enriched along with N doping, which leads to enhanced and better MB dye adsorption (in dark) as compared to a pure TiO$_2$ sample. Hence, an optimal combination of the anatase phase and N doping might lead to the formation of photocatalysts with best performance.

The proposed mechanism of MB dye photodegradation by the prepared samples is shown in Figure 11. Upon light irradiation, the photogenerated electrons jump to the conduction band whereas holes remain in the valence band. The photogenerated charges (electrons and holes) generate hydroxyl radicals by reacting with oxygen and water, respectively, which in turn acts as a strong oxidizing agent, degrading MB dye to other products such as CO$_2$, SO$_4^{2-}$, NH$_4^+$ and NO$_3^-$.

The possible reactions involved in the photodegradation of the MB dye simulated textile wastewater are presented in Equations (3)–(7).

\[
\begin{align*}
NT + h\nu \text{(light irradiation)} & \rightarrow NT(e^-_{CB}) + NT(h^+_{VB}) \\
NT (e^-_{CB}) + O_2 & \rightarrow O_2^- \\
NT (h^+_{VB}) + OH^- & \rightarrow OH \\
MB \text{ dye} + OH & \rightarrow CO_2 + H_2O + \text{Degradation products} \\
MB \text{ dye} + O_2^- & \rightarrow CO_2 + H_2O + \text{Degradation products}
\end{align*}
\]  

Figure 11. Mechanistic overview for photocatalytic degradation of MB dye simulated wastewater by NT samples.
4. Conclusions

Nitrogen-doped TiO$_2$ (NT) photocatalysts were successfully synthesized by a simply designed two steps synthesis procedure, employing urea as a nitrogen dopant and anatase phase-enriching agent. The analysis, specifically XRD, Raman and FTIR confirm that urea addition during the synthesis process acts as a doping source as well as anatase phase enhancer for the NT samples. The improved photocatalytic performance of NT samples as compared to pure TiO$_2$ sample is associated to the optimization of the photocatalytic active TiO$_2$ anatase phase, nitrogen content and surface area. Hence, the strategy of adding certain cheap additives, oriented towards achieving simultaneous doping as well as active phase generation, can be a cost effective and efficient approach to photocatalysts with high activity for wastewater treatment.

Supplementary Materials: The following are available online at https://www.mdpi.com/article/10.3390/app11178264/s1, Figure S1. UV Vis absorption spectra for the dye degradation employing (a) Pure TiO$_2$, (b) NT-1, (c) NT-2 and, (d) NT-3 sample; Figure S2. (a) UV Vis absorption spectra for the dye degradation employing standard TiO$_2$ P25 and (b) relative dye degradation curve; Figure S3. Adsorption Isotherm linear plot for (a) Pure TiO$_2$, (b) NT-1, (c) NT-2 and, (d) NT-3 samples.

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