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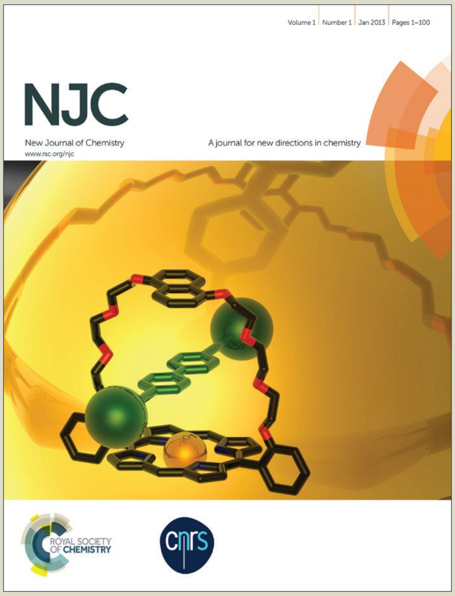

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Nitrogen-doped titanium dioxide (N-doped TiO_2) for visible light photocatalysis

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TiO_2 is an effective and well-known photocatalyst for water and air purification, but its practical applications in visible light-assisted chemical reactions are hindered mainly by its poor visible light absorption capacity. Nitrogen-doped TiO_2 (N-doped TiO_2) has attracted considerable attention as a photocatalyst, and rapid progress has been made in enhancing the photocatalytic efficiency of TiO_2 under visible light irradiation. N-doped TiO_2 exhibits broad absorption in the visible region, which can allow the utilization of a large part of the solar spectrum. This might be useful for environmental and energy applications, such as the photocatalytic degradation of organic pollutants, solar cells, sensors, and water splitting reactions. This review focuses on the major developments in the synthesis of N-doped TiO_2 and its possible applications to the photocatalytic degradation of organic pollutants and environmental remediation under visible light irradiation.

Introduction

Photocatalysis is a promising, environmentally friendly process for the conversion of solar energy to chemical energy or chemical conversion over a metal oxide nanostructure, such as the degradation of pollutants and hydrogen generation.[1] Metal oxide nanostructures, such as TiO_2, ZnO, CeO_2, and SnO_2, have attracted considerable research interest because of their great potential in the photocatalytic oxidation of organic pollutants.[2-7] Compared to other metal oxide nanostructures, TiO_2 has attracted attention owing to its high stability, photocatalytic activity, non-toxicity, and biocompatibility. On the other hand, TiO_2 is generally active under ultraviolet irradiation because of its wide band gap (band gap = 3.2 eV).[2,3,8,9]

TiO_2 has limited applications under visible light irradiation because of its poor light absorption ability and low charge separation efficiency under normal reaction conditions.[2,3,8] Therefore, considerable effort has been made to improve the light absorption of TiO_2 for efficient utilization of the solar energy spectrum.[2,3,9] For this purpose, many methodologies have been used to extend the photocatalytic activity of TiO_2 towards longer wavelengths (visible light), such as sensitization with organic dyes, where the dye acts as a photosensitizer and favors the injection of electrons into the conduction band (CB) of TiO_2, leading to better light absorption properties.[1-3,9,10] Another methodology is doping with transition metals, which inserts a new band into the original band gap of TiO_2 or modifies the CB or valence band (VB) of TiO_2 to enhance the light absorption properties.[1-3,9,10] In addition to the abovementioned techniques, a widely used methodology is the deposition of noble metal ions (Ag, Au, etc.) on the TiO_2 surface where the noble metal is exploited as a light harvester that helps to improve light absorption in the visible region.[3,9,10,11] On the other hand, the major drawbacks of the latter technique are the high cost of the reaction setup and the efficacy of the method. Noble metals, such as silver or gold, are toxic and quite expensive, which poses health hazard and increases the cost, respectively. Another important factor is the photocorrosion of metal-loaded photocatalysts during the visible light photocatalytic reaction. Therefore, replacing traditionally doped or metal-based TiO^2 photocatalysts[12-14] with non-metals doped photocatalysts, such as nitrogen-doped TiO_2, is becoming feasible and appears to enhance the photocatalytic activity of TiO_2 in the visible light region.[9,11]

Nitrogen doping is quite encouraging because of its comparable atomic size, small ionization energy and stability.[8,15,16] In addition, nitrogen doping only not modifies the crystal structure of TiO_2, but also suppresses the recombination rate of photogenerated electrons and holes, which leads to enhanced photocatalytic activity compared to bare TiO_2. Sato et al. prepared nitrogen-doped TiO_2 (N-doped TiO_2) by the calcination of commercial titanium hydroxide, but their results did not attracted much attention at that time.[17] Later, other reports were published. Asahi et al. reported that the nitrogen doping of TiO_2 increases the visible light photocatalytic activity of TiO_2.[18] Many studies also confirmed that nitrogen doping in TiO_2 easily enables the visible light photocatalytic activity of TiO_2 without reducing its activity under UV light.[15-18] Therefore, N-doped TiO_2 has attracted considerable attention for visible light applications and many reports on this topic have confirmed its visible light activity.[8,15,16] N-

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doping in TiO_2 is still a hot topic and is used widely as a highly visible light active photocatalyst for environmental remediation applications but further research will be needed to develop alternative pathways for preparing N-doped TiO_2 with excellent photocatalytic activity using facile techniques. Apart from the above discussion, stability of N-doped TiO_2 may also be an important issue of concern. D'Arienzo et al.[19] raised the issue of loss of N-doping due to treatments like calcinations, solubilization etc. which might result in decreased catalytic activity. Therefore, in order to prepare N-doped TiO_2 with high efficiency for catalytic reactions, the subsequent treatments in synthesis methodology should be optimized in such a way that it negates the loss of nitrogen from N-doped TiO_2.

This review summarizes the main characteristics and applications of N-doped TiO_2 and provides a comprehensive overview of current techniques and methodologies used to fabricate it. This review also focuses on previous studies and recent developments in the synthesis of N-doped TiO_2 by sol-gel methods, direct nitridization, electrochemical, and hydrothermal methods. The modified strategies to enhance the photocatalytic activity for the organic pollutant degradation under visible light irradiation are also discussed. The majority of applications of N-doped TiO_2 as a photocatalyst used in aqueous solutions are reviewed. A brief summary of the various applications regarding organic pollutant degradation is provided. Finally, suggestions regarding the future prospects and possibilities in this area of research are proposed and discussed.

Origin of visible light absorption and photoexcitation mechanism over N-doped TiO_2

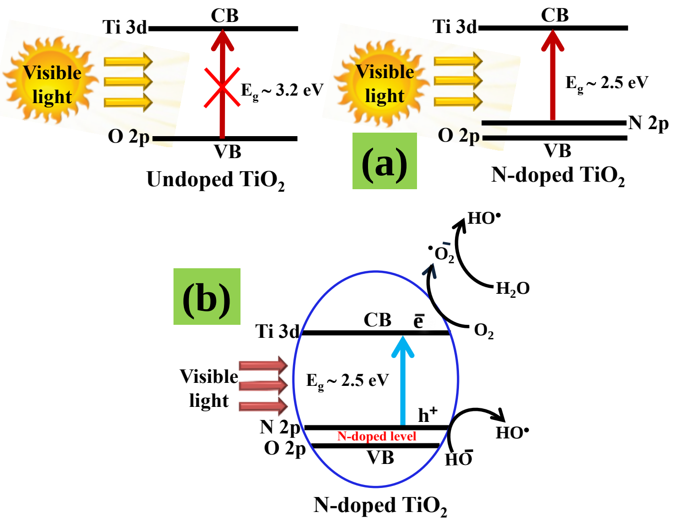

Fig. 1. (**a**) Energy level diagrams for undoped and N-doped TiO_2 and (**b**) possible reaction mechanism for the photocatalytic degradation of organic pollutants by N-doped TiO_2 under visible light irradiation.

Generally, photocatalysis is based on the generation of electron-hole pairs upon irradiation with light.[1-4] The electron migrates from the valence band to the conduction band, leaving behind a hole in the valence band, which participates in redox reactions with adsorbed organic species and adsorbed molecular oxygen.[1-6] On the other hand, the generation of electrons in the conduction band and holes in the valence band under visible light irradiation is not feasible owing to the wide band gap of TiO_2 (~3.20 eV).[2,3] The incorporation of nitrogen into the TiO_2 lattice, leads to the formation of a new mid gap energy state, i.e., the N 2p band above the O 2p valence band, which eventually decrease the band gap of TiO_2 (to ~2.5 eV) and shifts the optical absorption to the visible light region.[9,15] Therefore, it is possible for the electrons to migrate from the valence band to the conduction band upon absorbing visible light, which leads to the visible light activity of N-doped TiO_2 (Fig. 1a).[9,15-18] The proposed schematic diagram (Fig. 1b) represents a reduced band gap state after N doping and photocatalytic degradation reactions under visible light irradiation. The figure shows the generation of electrons in the conduction band and holes in the valence band under visible light illumination. These electrons in the conduction band accumulate on the catalyst surface, and are then scavenged by oxygen molecules, either dissolved in water or in the atmosphere to yield highly oxidative species, such as superoxide radical anions and hydroxyl radicals.[1-5,20] These highly reactive radicals are responsible for the degradation of organic pollutants. The holes generated in the VB are scavenged by OH^- ions to generate highly oxidative species, such as hydroxyl radicals ($HO^\bullet$), which are highly reactive and responsible for the degradation and mineralization of organic pollutants.[1-5,15]

Possible doping mechanisms for the introduction of nitrogen impurities in interstitial and substitutional sites in TiO_2

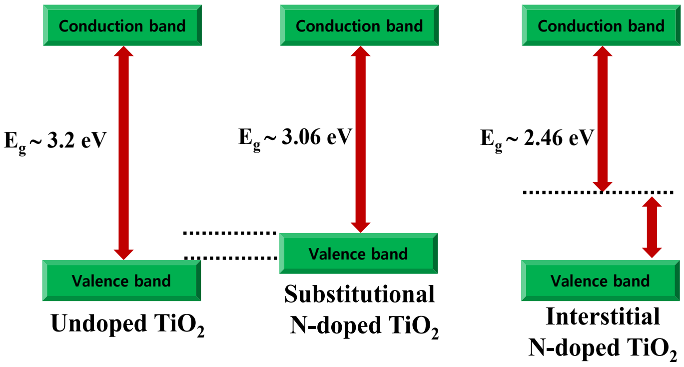

Fig. 2. Schematic diagram showing the valence and conduction bands of undoped and N-doped TiO_2.

Nitrogen doping induces significant improvements in the optical absorption and photocatalytic degradation capacity of TiO_2 in the visible light region.[21] Despite this, the mode of nitrogen doping in the TiO_2 lattice is unclear, i.e., whether nitrogen doping is substitutional or interstitial, which is essential for its visible light photocatalytic activity. Substitutional doping leads to surface modification via the attachment of nitrogen by interactive forces, such as dipole-dipole interactions, van der Waals forces, London forces, or electrostatic interactions.[9,15,17,18] On the other hand, interstitial doping affects the lattice structure of N-doped TiO_2. Asahi et al. reported a possible way of incorporating nitrogen into the TiO_2 lattice using a first-principle calculation method.[18] The proposed method included substitutional N-doping, substitutional

NO-doping, interstitial N-doping, and interstitial NO-doping. In a similar report, Dunnill et al. showed that the incorporation of nitrogen into the TiO_2 structure occurs via substitutional and interstitial means (Fig. 2).[9,15] They reported that substitutional doping involves oxygen replacement, whereas interstitial doping involves the addition of nitrogen into the TiO_2 lattices.[15] Substitutional doping reduces the band gap (~3.06 eV) but to a lesser extent to that achieved by interstitial doping (~2.46 eV). The location of nitrogen doping in TiO_2 is critical to its behavior as a photocatalyst, but there is controversy regarding which position is most beneficial. Many reports have shown that a combination of both substitution and interstitial doping generally occurs during nitrogen doping of the TiO_2 lattices.[16,22] The presence of nitrogen can alter the band structure or suppresses the recombination efficiency of the photo-generated electron-hole pairs, resulting in an enhanced photocatalytic capacity of TiO_2 in the visible light region.[9,15,18]

Different methodologies for the preparation of N-doped TiO_2

Recently, a large number of physical and chemical methods have been used to incorporate nitrogen into the TiO_2 lattices (Fig. 3), which include ball milling,[23] sputtering,[24] plasma or ion implantation,[25] sol-gel method,[26] solvothermal,[27] hydrothermal,[28] direct hydrolysis of organic/inorganic salts,[29] and the oxidation of titanium nitride.[9] Among them, most common and efficient methodology is the direct synthesis of TiO_2 in a nitrogen environment or an oxygen treatment of titanium nitride.[18,30] The sources of nitrogen generally used for the synthesis of N-doped TiO_2 is nitrogen dioxide, tert-butylamine, ammonia, hydrazine, triethylamine, urea, and thiourea.[9,15,16,23-30]

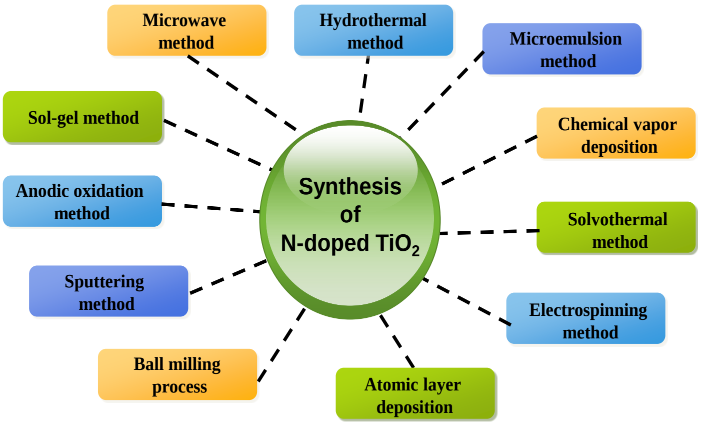

Fig. 3. Schematic diagram showing the different synthetic routes for the synthesis of N-doped TiO_2.

Pioneering work in the field of N-doped TiO_2 showed that nitrogen doping in TiO_2 leads to a significant decrease in the band gap of TiO_2, making it active in the visible light region.[17,18] First-principles calculations and X-ray photoemission spectroscopy showed that nitrogen doped into the substitutional sites of TiO_2 is indispensable for band gap narrowing and improving the photocatalytic activity. N-doped TiO_2 exhibited enhanced photocatalytic ability for the degradation of methylene blue and gaseous acetaldehyde compared to pure TiO_2.[18]

Different synthetic routes for the preparation of N-doped TiO_2, such as electrospinning, have shown promising results.[31] Electrospinning using polyvinylpyrrolidone (PVP) as the nitrogen source allowed a broader absorption of TiO_2. PVP plays a dual role, first preserving the high-energy facets of TiO_2 during synthesis as well as final doping during its decomposition. The nitrogen atom is substituted into the oxygen sites, leading to a decrease in the band gap of TiO_2. The narrower band gap of TiO_2 extends its absorption spectrum to the visible region, and when applied to photocatalytic degradation reactions, it enhanced the photooxidation of arsenite (III) to arsenate (V) under visible light irradiation.[32]

Spherical-shaped, N-doped TiO_2, which was synthesized by Sathish et al. using $TiCl_3$ as a precursor via a simple chemical method, was found to be an effective way of nitrogen doping due to the mixing of N 2p states with O 2p states on top of the valence band or the formation of a N-induced mid-gap level.[32] N-doped TiO_2 strongly absorbed visible light due to the narrow band gap of TiO_2, resulting in the generation of electrons and holes under visible light irradiation. The photocatalytic decomposition of methylene blue carried out in the visible light region and N-doped TiO_2 photocatalysts exhibited higher photocatalytic activity than that of bare TiO_2 in the visible region.[32]

TiO_2 can be synthesized by a large number of different precursors using a range of techniques.[33,23-27] The effects of the precursor source for TiO_2 and its concentration would be an interesting area of study. Titanium tetraisopropoxide and titanium tetrachloride are generally used as the sources for TiO_2 synthesis, whereas thiourea is used as the nitrogen source for the synthesis of N-doped TiO_2. N-doped TiO_2 is synthesized via a solution-based method using titanium tetraisopropoxide/titanium tetrachloride with thiourea. Light absorption studies revealed a new absorption shoulder at 400-520 nm corresponding to nitrogen.[15] A plot of the modified Kubelka-Munk function vs. the energy of absorbed light showed that the band gap decreased from 2.99 to 2.19 eV due to the increasing concentrations or ratio of titanium tetraisopropoxide/titanium tetrachloride to thiourea from 0.35 and 1.40 M to 0.56 and 2.24 M. This resulted in significant band gap narrowing of 0.08 eV for TiO_2 synthesized from titanium tetrachloride, whereas TiO_2 synthesized by titanium tetraisopropoxide showed only 0.04 eV band gap lowering. Most of the N-doped TiO_2 photocatalysts enhanced the photocatalytic degradation of 4-chlorophenol under artificial visible light irradiation, and 30% mineralization was achieved during the photocatalytic reaction for N-doped TiO_2 synthesized from titanium tetrachloride. This suggested that among the N-doped TiO_2 prepared by different precursors, titanium tetrachloride and thiourea combination exhibited the highest photocatalytic activity.[33]

In another major development, different types of organic compounds as the nitrogen source, such as triethylamine, urea, thiourea, and hydrazine hydrate, were used for the synthesis of N-doped TiO_2.[34] Absorption studies revealed a shift in the absorption edge to a lower energy and stronger absorption in the visible light region. Most N-doped TiO_2 showed enhanced photocatalytic degradation capacity for the degradation of Rhodamine B in visible light irradiation compared to undoped TiO_2 and Degussa TiO_2. Among them, N-doped TiO_2 using triethylamine as the nitrogen source exhibited the highest photocatalytic activity for the photodecomposition of 2,4-dichlorophenol.[34]

In addition to normal chemical routes, hydrothermal processing and subsequent heating in a NH_3 environment can be used for the facile synthesis of N-doped TiO_2 photocatalysts with different doping levels. The technique is simple because the level of nitrogen doping in a TiO_2 crystal can be controlled easily according to the requirements of the reaction system. Wang et al.[35] applied density functional theory to their synthesized N-doped TiO_2 photocatalysts to examine the mechanism of photocatalysis.[35] Their calculations showed that nitrogen doping leads to an add-on shoulder on the edge of the valence band, localized N 2p levels above the valence band maximum and 3d states of Ti^{3+} below the conduction band. The results revealed a good correlation with the X-ray photoelectron spectroscopy (XPS) and UV-visible absorbance spectroscopy data. The doped TiO_2 photocatalyst exhibited enhanced photocatalytic activity for the degradation of methyl orange dye under visible light irradiation.[35] In a similar study, N-doped TiO_2 with dominant [001] facets was synthesized using a hydrothermal method. The reactive facets of TiO_2 play important roles in the photocatalytic reaction, and the fabrication of different facets of TiO_2 can allow the selective band gap engineering of TiO_2.[36] TiO_2 is normally dominated by [101] facets because of its lower surface energy compared to [001] facets. N-doped TiO_2 with dominant [001] facets showed enhanced photocatalytic behavior for the photodegradation of methylene blue compared to bare TiO_2 under visible light irradiation. The enhanced photocatalytic activities of N-doped TiO_2 were attributed to the synergistic effects of many factors, such as the crystal phase, morphology, nitrogen doping, and optical response. The morphology and nitrogen doping are considered to be more significant factors than the crystal phase and optical response.[36]

Recently, a strategy to couple a binary structure with nitrogen doping was designed to the synthesis of anatase/rutile nanoparticles with a 9-fold increase in visible light photocatalytic activity compared to pure TiO_2.[37] Gai et al. prepared N-doped TiO_2 photocatalysts via a one-pot synthetic route (solvothermal method) with high crystallinity. Nitrogen doping not only modified the band structure of TiO_2 to make it more responsive to visible light, but also suppressed charge recombination, resulting in TiO_2 with enhanced photocatalytic activity compared to undoped TiO_2. The prepared N-doped TiO_2 photocatalysts exhibited enhanced photocatalytic activity for the photodegradation of methyl orange and a 4-chlorophenol solution under visible light illumination compared to the undoped TiO_2 photocatalyst.[37]

The sol-gel process is a versatile process for preparing N-doped TiO_2 because it does not require sophisticated instrumentation.[9,15,16] The incorporation of an active dopant in the sol during the gelation stage allows direct interactions of the doping elements with the support, giving a composite system high catalytic or photocatalytic properties.[22] Zhou et al.[38] fabricated a mesoporous N-doped TiO_2 photocatalyst using the above mentioned method with ammonium nitrate as the nitrogen source.[38] The absorption studies revealed significant enhancement in absorbance in the visible region 400-550 nm, which is the typical absorption feature of N-doped TiO_2. The photocatalytic activity of N-doped TiO_2 was evaluated by the photocatalytic degradation of aqueous solutions of methylene blue. The results revealed excellent photodegradation efficiency for the catalytic degradation of methylene blue compared to undoped TiO_2.[38] The different types of interactions between the nitrogen dopant sources and TiO_2 precursors during sol–gel synthesis might also lead to N-doped TiO_2 with different physical and chemical properties.[15,17,18] The nitrogen source, 1,3-diaminopropane, and titanium tetraisopropoxide showed an enhanced response to visible light at selective temperatures.[39] When the properties were evaluated at different temperatures, differential scanning calorimetry showed that crystallization occurs below 500 °C, and a high temperature treatment above 600 °C resulted in reduced visible light absorption. The sample at 500 °C showed significant absorption in the visible region and the best photocatalytic activity. XPS showed that nitrogen remained within the TiO_2 lattice at higher temperatures. This led to the formation of N 2p bands between the valence band and conduction band of TiO_2, which might be responsible for visible light absorption.[34] The photocatalytic degradation of methylene blue and 4-chlorophenol was carried out under visible light irradiation. The N-doped TiO_2 calcined at 500°C showed enhanced photocatalytic activity because of the low rate of the recombination process.[39]

In a similar study, N-doped TiO_2 was synthesized at low temperatures using titanium tetraisopropoxide, ethyl methylamine and hydrogen peroxide to determine the structural properties and N doped sites.[40] Fourier transform infrared spectroscopy revealed a flat band below ~800 cm^{-1}, which is a clear signature of nitrogen incorporation in TiO_2. High resolution transmission electron microscopy showed that in the case of N-doped TiO_2, the lattice fringes appear to be distorted incoherently compared to undoped TiO_2. This might be due to the possible interactions between nitrogen and TiO_2 via dopant-dopant interactions. XPS also showed that nitrogen was doped substitutionally in the TiO_2 lattice.[29,31] The light absorption properties revealed extended tailing of the absorption edge towards the visible region upon nitrogen doping. N-doped TiO_2 exhibited excellent photocatalytic activity for the photodegradation of methylene blue under visible light irradiation compared to undoped TiO_2.[40]

Recently, Wang et al.[41] reported the same method for the preparation of N-doped TiO_2. The as-synthesized N-doped TiO_2 was in the anatase phase and the mean crystallite size of the particles was approximately 15 nm. Binding energy analysis showed that the nitrogen atoms were incorporated into the TiO_2 surface, mainly as interstitial nitrogen and molecularly chemisorbed N_2 molecules, and a small amount were incorporated as substitutional nitrogen atoms. UV-Vis diffuse reflectance/absorption studies revealed a significant increase in absorption as well as a decrease in the band gap from 3.12 to 2.22 eV for pure TiO_2 and N-doped TiO_2, respectively. The enhanced light absorption in the visible range and band gap narrowing of the N-doped TiO_2 provides further evidence of nitrogen doping in the TiO_2 lattice, which can induce local states above the valence band edge. The prepared N-doped TiO_2 exhibited enhanced photocatalytic activity for the degradation of methyl orange under visible light irradiation compared to pure TiO_2.

Cheng et al. reported the formation of N-doped TiO_2 using a simple solution-based method via the addition of ammonia water.[42] Nitrogen doping could inhibit the phase transformation of TiO_2, which helped enhance light absorption in the visible region. From XRD, the mean crystal sizes of the pure TiO_2 and N-doped TiO_2 was calculated to be 8 and 6 nm, respectively. The difference in crystal size may be due to N doping. The absence of additional peaks in the XRD pattern showed that N occupied either the interstitial positions or the substitutional sites of the TiO_2 crystal structure. In XPS, the peak at 399.5 eV was assigned to the interstitial N, i.e., the formation of an N-Ti-O state, as well as other small peaks at 397.4 and 401.7 eV, corresponding to substitutional nitrogen in the Ti-N structure. This provides further evidence of the existence of both interstitial and substitutional nitrogen doping in the TiO_2 lattice. This multi-type nitrogen doping might induce the formation of a new energy level in the forbidden band of TiO_2, which is related to the enhancement of the photocatalytic activity in the visible range. The photocatalytic experiments for the degradation of phenol under simulated sunlight revealed N-doped TiO_2 to have much higher degradation efficiency than undoped TiO_2. The high catalytic efficiency of the former can be attributed to the small crystallite size, high crystallinity and intense light absorption in the visible light

Table 1. Synthesis of N-doped TiO_2 via different methods and its photocatalytic activity for the degradation of various types of organic pollutants.

Synthesis methods	Photocatalyst	Organic pollutants	References
Solvothermal method	N-doped anatase TiO_2	Methylene blue and methyl orange	[27]
Mixing method	N-doped TiO_2	2-propanol	[50]
Chemical vapor deposition	N-doped TiO_2	2-chlorophenol	[51]
Post-calcination method	N-doped TiO_2	Ethyl benzene, o,m,p-xylenes)	[52]
Hydrothermal	N-TiO_2/C	Methylene blue	[28]
Microwave assisted method	N-doped TiO_2	Malathion	[53]
Electric field and heat treatments	N-doped TiO_2 composite	Methylene blue	[54]
Calcination process	N:TiO_2	Rhodamine B and atrazine	[55]
Anodic oxidation method	N-doped TiO_2	Organophosphorus pesticide acephate	[56]
Sol-gel method	N-doped TiO_2	Methylene blue	[57]
Precipitation methods	N-doped TiO_2	Toluene	[58]
Solution method	N-TiO_2	Rhodamine B andciprofloxacin	[59]
Sol-gel method	N-doped TiO_2/ACF	Methyl orange	[41]
Direct nitridization method	N-doped TiO_2	Methylene blue	[43]
Electrochemical method	N-TiO_2	Methylene blue	[44]
Colloidal crystal-templating method	N-doped TiO_2	Rhodamine B	[60]
Electrospinning method	N-doped TiO_2	Photooxidation of arsenite (III) to arsenate (V)	[31]
Chemical method	N-TiO_2	Methylene blue	[32]
Solution based method	N-doped TiO_2	4-chlorophenol	[33]
Microemulsion-hydrothermal method	N-doped TiO_2	Rhodamine B	[34]
Sol-gel method	N-doped TiO_2	Methylene blue	[38]
Hydrothermal method	N-doped TiO_2	Methyl orange	[35]
Solvothermal method	N-doped TiO_2	Methyl orange and 4-chlorophenol	[37]
Hydrothermal method	N-doped TiO_2	Methylene blue	[38]
Sol-gel method	N-doped TiO_2	Methylene blue	[40]
Solution based method	N-doped TiO_2	Phenol	[42]
Sol-gel method	N-doped TiO_2	Methylene blue and 4-chlorophenol	[39]
Electrospinning method	N-doped TiO_2	Methylene blue	[61]
Atomic layer deposition	N-doped TiO_2	Hydrogen production	[62]
Vapor-thermal method	N-doped TiO_2	Methyl orange, methylene blue, and Rhodamine	[63]
Sol-gel method	N-doped TiO_2	Methylene blue	[64]
RF-sputtering process	N-doped TiO_2	Chlortetracycline	[45]
Magnetron sputtering	N-doped TiO_2	Benzamide	[46]
Atomic layer deposition	N-doped TiO_2	Stearic acid	[47]
Atomic layer deposition	N-doped TiO_2	Photocurrent analysis	[48]
Pulse laser deposition method	N-doped TiO_2	Methylene blue and methylene orange	[49]
Low-energy ion implantation	N-doped TiO_2	Methylene blue	[65]
Sol-gel process	N-doped TiO_2	Reactive black and Rhodamine B	[66]
Plasma assisted metal organic CVD	N-doped TiO_2	2-chlorophenol	[67]

region.[42] Table 1 lists the methods for preparing various types of N-doped TiO_2 as well as their different photocatalytic applications.

Hu et al.[43] reported the colloidal N-doped TiO_2 prepared by low-temperature direct nitridization in a triethylamine solution during the hydrolysis of tetrabutyltitanate, followed by an acidic peptization method. The acid concentration and peptization time could effectively influence the anatase and rutile phase transformation of TiO_2, which helps enhance light absorption in the visible light region. The N 1s binding energy spectrum confirmed the substitutional nitrogen doping of lattice oxygen in the TiO_2 crystals. The optical properties of N-doped TiO_2 showed that the light response in the range, 400–500 nm, was improved clearly by nitrogen doping, which facilitates the absorption of photons under visible light irradiation. The as-synthesized N-doped TiO_2, which contains 63.1% anatase, exhibited the highest photocatalytic activity for the degradation of methylene blue under visible light irradiation compared to pure TiO_2, which is due to the synergistic effect between the anatase and rutile phases of TiO_2.

In another development in the field of TiO_2 modification by nitrogen doping, Siuzdak et al.[44] fabricated highly ordered and vertically-oriented N-doped TiO_2 tubes using an electrochemical method. The presence of nitrogen in TiO_2 was confirmed by a range of spectroscopic techniques. Furthermore, the presence of nitrogen in the TiO_2 crystal resulted in a narrowing of the band gap of pure TiO_2. Photoluminescence spectroscopy, the photocatalytic behavior and steady-state photocurrent studies showed that nitrogen doping not only modified the band structure of TiO_2 to make it more responsive to visible light, but also suppressed charge recombination of the photogenerated electrons / holes pairs, resulting in an enhancement of the photocatalytic activity of the N-doped TiO_2 compared to pure titania.

Delegan et al.[45] incorporated N into the TiO_2 lattice by controlling the nitrogen-to-argon mass flow rate ratio in the deposition chamber of a radio frequency sputtering process. The nitrogen content in the doped TiO_2 was examined further by XPS and found to be 0.2-6.2 atomic weight percent. The band gap (E_g) obtained from the absorption spectra showed that the optimal nitrogen level (0.4 at. % N) effectively reduced the band gap of TiO2 from 3.2 to 2.3 eV and that any further increase in nitrogen doping did not have any additional effect on the band gap. The effect of the N content on the photoactivity of N-doped TiO_2 films was observed by the photocatalytic decomposition of chlortetracycline under standard solar irradiation. The degradation results showed that the narrowest band gap N-doped TiO_2 with optimized N-doping induced the highest rate of degradation compared to the other samples.

Chen et al.[46] prepared N-doped TiO_2 films on aluminum substrates by reactive magnetron sputtering with an O_2/N_2 mixture and further studied its photocatalytic activity for the degradation of benzamide under a 20 W low-pressure mercury lamp. The photocatalytic results showed that the catalyst obtained at a ratio of 80% $N_2/(O_2 + N_2)$ air flow has the highest catalytic activity compared to pure TiO_2.

Pore et al.[47] synthesized N-doped TiO_2 photocatalyst films with a reduced band gap by atomic layer deposition using $TiCl_3$, ammonia and water as the initial precursors. The estimated band gap calculated from a plot of $(\alpha h\nu)^{1/2}$ versus eV was lower than that of TiO_2, which is related to nitrogen doping through the mixing of N 2p and O 2p states of nitrogen and TiO_2. The influence of nitrogen doping on the photocatalytic activity of N doped TiO_2 films were examined by the degradation of stearic acid in UV and visible light irradiation. The degradation results showed that nitrogen doping effectively improves the photocatalytic activity of N-doped TiO_2 films.

Cheng et al.[48] synthesized N-doped TiO_2 films on silicon substrates by atomic layer deposition and examined the photocurrent response under visible light irradiation. They reported that the optimal nitrogen doping was 1.2 weight percent, which helped inhibit the anatase to rutile transformation, which is advantageous for high catalytic activity. They also reported that either too low or high nitrogen doping results in inefficient visible light absorption as well as rapid charge carrier recombination, which may give poor photocatalytic properties.

Zhao et al.[49] employed a pulse laser deposition method to prepare N-doped TiO_2 thin films and further observed its degradation efficiency under visible-light for the degradation of methylene blue and methylene orange. N-doped TiO_2 achieved 47.2 and 46.4% degradation of methylene blue and methyl orange, respectively.

Applications of N-doped TiO_2

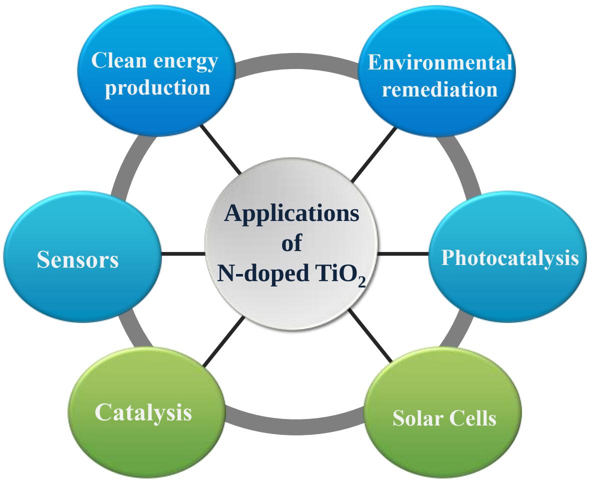

Fig. 4. Possible applications of N-doped TiO_2.

In general, the improved photocatalytic activities of N-doped TiO_2 is due to the synergistic effects of many factors, such as dominant facets, morphology, defects, crystal phase, optical response, and nitrogen doping. Among them, nitrogen doping appears to be the most significant and dominant factor compared to the others. Modification of the crystal structure of TiO_2 by nitrogen doping not only reduces its band gap, but also suppresses the recombination rate of the photogenerated electrons-holes, which eventually leads to enhanced photocatalytic activity of N-doped TiO_2 compared to bare TiO_2.

Asahi et al.[18] reported that N-doped TiO_2 has much higher photocatalytic activity for the degradation of methylene blue and gaseous acetaldehyde under visible light irradiation (wavelength <

500 nm). Similarly, Sato et al.[17] showed that yellow-colored TiO_2 obtained by calcining commercial titanium hydroxide at 400 °C has higher photocatalytic activity towards the oxidation of CO, ethane, and oxygen isotope under the visible light irradiation than bare TiO_2. Different methodologies adopted for the production of N-doped TiO2 by several groups showed that the modified TiO_2 has better photocatalytic properties compared to pure one. Burda et al.[21] produced N-doped TiO_2 from the direct amination of TiO2 and reported that 6-10 nm-sized N-doped TiO_2 particles exhibited enhanced photocatalytic activity for the degradation of methylene blue under visible light irradiation. Similarly, Shifu et al.[23] reported that the mechanical grinding of TiO_2 in an aqueous ammonia solution successfully doped TiO_2 with nitrogen, and the resulting catalyst showed better photo degradation efficiency towards the degradation of methylene blue compared to bare TiO_2 under visible light. In a powdered catalyst, the thin films also showed improved photocatalytic properties after nitrogen doping. Prabakar et al.[24] reported that N-doped TiO_2 thin films prepared by sputtering on glass substrates displayed improved photocatalytic decomposition of methanol under visible light irradiation compared to the undoped TiO_2 film. N-doped TiO_2 films obtained by plasma-enhanced chemical vapor deposition also showed good photocatalytic activity for the decomposition of organic compounds and photoinduced hydrophilicity under visible light irradiation.[25] Yang et al.[27] reported that N-doped TiO_2 obtained via a solvothermal method exhibited excellent photodecomposition ability for the degradation of methylene blue (MB) and methyl orange (MO) under visible light irradiation. Wang et al.[28] showed that N-doped TiO_2 nanoparticles prepared by a post-thermal treatment has enhanced visible light photocatalytic activity for the degradation of methylene blue. Another methodology for the preparation of N-doped TiO_2 involving acid-catalyzed hydrolysis resulted in a modified catalyst with very high photocatalytic activity in both UV and visible light regions towards the degradation of phenol compared to bare TiO_2.[29] Sathish et al.[32] reported that the N-doped TiO_2 nanocatalyst synthesized by the chemical method showed largely improved photocatalytic activity for the decomposition of methylene blue compared to the Degussa P25 TiO_2 photocatalysts in both the UV and visible region. Sakthivel et al.[29] also used a chemical method for N-doped TiO_2 and reported excellent mineralization of 4-chlorophenol under visible light ($\lambda \geq 455$ nm) irradiation. Cong et al.[34] also showed that N-doped TiO_2 nanocatalysts synthesized through a microemulsion hydrothermal method exhibited enhanced photocatalytic activity for the degradation of organic pollutant, Rhodamine B and 2,4-dichlorophenol, compared to the undoped TiO_2 and Degussa P-25 photocatalysts in visible light irradiation ($\lambda > 420$ nm). The high performance was attributed to nitrogen doping, which inhibits the recombination of the photoinduced electrons, and improves the photocatalytic efficiency of N-doped TiO_2. The studies of photocatalysis on different exposed facets of TiO_2 gave different activities. Zhang et al.[31] reported that crystalline N-doped TiO_2 with exposed high-energy facets obtained via an electrospinning method displayed superior photooxidation of arsenite (III) to arsenate (V) in both the UV and visible light regions. Similarly, Shi et al.[32] reported that N-doped TiO_2 plates with dominant {0 0 1} facets had superior photocatalytic activities for the degradation of methylene blue under visible light irradiation ($\lambda > 420$ nm). The N-doped TiO_2 nanorods with good crystallinity reported by Gai et al.[37] exhibited higher catalytic activity for the decomposition of methyl orange and 4-chlorophenol compared to the nanoparticle counterparts under UV and/or visible light illumination. Therefore, from the above discussion, it is clear that N-doped TiO_2 can be synthesized by a wide variety of routes and can be used for a wide range of applications (Fig. 4), such as the degradation of colored and non-colored organic pollutants (dyes), air purification, sensors, solar energy conversion, and photovoltaics owing to its nontoxicity, ease of synthesis, low cost, and high chemical stability.[9] Among these, some of the applications developed successfully for practical applications using N-doped TiO_2 are as follows:

i. Industrial textile effluent degradation
ii. Self-cleaning
iii. Air purification
iv. Tooth whitening
v. Water treatment system
vi. Environmental remediation

Summary and future prospects

In summary, N-doped TiO_2 has been synthesized and used for a range of applications. N-doped TiO_2 found an alternate route for the noble metal-doped TiO_2, which is generally visible light active. The material not only effectively reduces the band gap by forming a mid-gap state, but also decreases the recombination of electrons and holes, and is quite economical. Reports on the origin of visible light photocatalysis in N-doped TiO_2 flooded in after the first-principle calculations, and Asahi et al.[18] reported that N-doped TiO_2 have improved photocatalytic behavior compared to bare TiO_2 under visible light irradiation. The introduction of nitrogen as an impurity in a TiO_2 crystal is an efficient way of improving the solar light harvesting ability and photocatalytic activity of N-doped TiO_2. N-doped TiO_2 with improved visible light photocatalytic activity can be produced by a number of simple synthetic methods, such as sol-gel method, plasma or ion implantation, solvothermal, ball milling, sputtering, hydrothermal, and the direct hydrolysis of organic/inorganic salts. To produce nitrogen dioxide, tert-butylamine, ammonia, hydrazine, triethylamine, urea, and thiourea have been used as the nitrogen source for doping TiO_2.

Nitrogen is still the best dopant for TiO_2 compared to other non-metal dopants, such as sulfur, iodine, and fluorine. N-doping helps improve the photocatalytic activity of TiO_2 under visible light irradiation for environmental remediation and other applications. In contrast to bare TiO_2, N-doped TiO_2 shows superior photocatalytic performance for the degradation of organic pollutants, such as methylene blue, methyl orange, 2-chlorophenol, Rhodamine B, atrazine toluene, and 4-chlorophenol, and there are wide range of prospects, which will be the subject of future research. Therefore, the synthesis of N-doped TiO_2 photocatalysts by different routes and their applications to the visible light photodegradation of pollutants is vast.

Although N-doped TiO_2 showed superior photocatalytic activity that covered the maximum part of the solar energy spectrum, which is a satisfactory result from an application point of view, but the stability is still questionable. The following limitations provide scope for future research to produce highly efficient N-doped TiO_2:

- Controlling substitutional or interstitial doping in the TiO_2 lattice may produce interesting results in terms of the catalyst efficiency because the location of nitrogen in the lattice is critical for the photocatalytic efficiency. Therefore, optimization needs to be performed by trial and error experiments to determine the effects of the experimental parameters on the nitrogen doping behavior on the structural behavior of TiO_2.
- For a practical application point of view, the efficiency of N-doped TiO_2 under a variety of illuminations, ranging from natural sunlight to artificial visible light irradiation conditions, should be studied. In addition, a study of the realistic wastewater degradation ability of the N-doped photoctalysts is needed.
- The co-doping of N-doped TiO_2 with other metals and non-metals can be an interesting area of research. The fabrication of different nanostructures, such as nanowires, nanotubes, spheres, hollow spheres etc., can provide N-doped TiO_2 with hitherto unreported properties, which can have a huge impact on the photocatalyst efficiency.
- The precise mechanism of band gap reduction by N-doped TiO_2 is still unclear. Another factor is the stability of the N-doped TiO_2 during the photo electrolysis of water. These might be the subject of future research.
- The fabrication of N-doped TiO_2 with excellent photocatalytic activities using simple facile techniques utilizing green routes can be a promising field for a range of applications and pollution free approach.

Therefore, it is expected that N-doped TiO_2 with unique properties and characteristics will be synthesized and solve various wastewater treatment, energy and environment problems.

Declaration of interest

The authors report no conflicts of interest. The authors alone are responsible for the content and writing of the paper.

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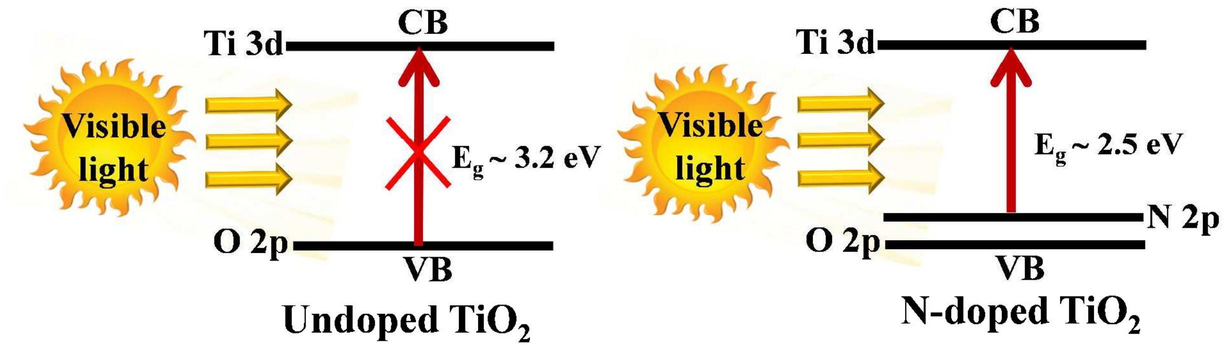
Graphical Abstract



Energy level diagrams for undoped and N-doped TiO_2 for visible light induced photocatalytic application.