A NOVEL APPROACH TO DEVELOP HIGHLY ACTIVE N-DOPED TiO₂ PHOTOCATALYST BASED ON PROPERTIES OF NITROGEN PRECURSOR

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Abstract
This paper reports the preparation of N-doped TiO₂ nanoparticles with an average of size ca. 9.8 nm synthesized by a controlled sol–gel reaction followed by calcinations at 400 °C. Triethylamine, triethanolamine, diisopropylamine were used to dope titania to prepare N-doped titania. By coupling structural (by X-ray diffraction, RAMAN spectra) and morphological (HRTEM, BET) characterizations with spectroscopic analyses (EPR and XPS), it was found that the nature of the nitrogen precursor affect photocatalytic behaviour of the synthesized nitrogen doped titania nanoparticles. The photocatalytic efficiency of a TiO₂ photocatalyst depends not only on the electronic properties of the materials. The availability of active sites on the material surface also plays a major role in the ability of the photocatalytic material to degrade organic contaminants. Nitrogen precursor with large surface area possesses more surface hydroxyl groups and hence produces more photoactivity. The photocatalytic activity was tested using a UV irradiation source with regard to decomposition of the dye fluorescein. In the case of fluorescein degradation the disappearance of the green colour was measured directly by means of fluorescence spectrophotometer. All N-doped samples produced a better removal of the dye fluorescein than the undoped and commercial samples.

Keywords: Titania, Nitrogen doped Titania, Photocatalyst, Photocatalysis, Fluorescein.

1. Introduction
In 1972 Fujishima and Honda published an article in Nature that demonstrated the powerful semiconductor capabilities of TiO₂ in the splitting of water in a photo electrochemical cell. Their work ignited a revolution in the world of semiconductor research [1]. Later in 1977, Frank and Bard demonstrated titanium dioxide’s unique properties for environmental remediation through the reduction of CN⁻ in water [2, 3], and in 1983 Ollis and co-workers used TiO₂ for the mineralisation of organic pollutants [4, 5]. In the 1990’s, Graetzel demonstrated use of TiO₂ in dye sensitized solar cell [6]. Thereafter TiO₂ became one of the most internationally researched semiconductor materials. However, major drawback of TiO₂ photocatalysis is the large band gap (3.2 eV for anatase phase). Titanium dioxide can only be activated upon irradiation with a λ<390 nm, limiting its use under solar radiation [7]. Ultraviolet light makes up 3 – 5 % of the solar spectrum, whereas the spectrum consists of ~ 40 % visible light. Therefore, in order to utilise TiO₂ to its full potential it is necessary to decrease the band gap size facilitating visible light absorption. Non-metal doping has shown great promise in achieving visible light activated photocatalysis, with nitrogen being the most effective dopant. Metals have also been employed to tune the electronic structure of TiO₂-based material [8-10]. The photocatalytic reactivity of metal-doped TiO₂ depends on many factors [11], and metal doping can result in thermal instability and increased carrier trapping. There are at least two factors to consider while employing dopants to change the optical responses of TiO₂. First, it is desirable to maintain the integrity of the crystal structure of the photocatalytic host material; second requirement
is to produce favourable changes in its electronic structure. The crystal structure of a material is directly related to the ratio of the cation and anion sizes in the crystal lattice. While it appears easier to substitute the Ti\(^{4+}\) cation in TiO\(_2\) with other transition metals, it is more difficult to replace the O\(^2-\) anion with other anions due to differences in charge states and ionic radii. However, the inherent lattice strain in nanometer-sized materials provides an opportunity to dope TiO\(_2\) to a larger extent.

The earliest report on visible-light-active N-doped TiO\(_2\) is dated back to 1986 [12]. In 2001 Asahi et al. [13] prepared TiO\(_2\)-N\(_x\) films by sputtering the TiO\(_2\) target in a N\(_2\) (40%)/ Ar gas mixture and then annealing at 550\(^\circ\)C in N\(_2\) gas for 4h. This then marked the beginning of growth of interest in nitrogen doped titania. In 2003 Irie et al. [14] prepared yellow to green coloured TiO\(_2\)-N\(_x\) powders by annealing anatase TiO\(_2\) powder under NH\(_3\) flow at 550, 575 and 600 \(^\circ\)C. Zhang et al. in 2004 discussed the mechano-chemical synthesis of nitrogen doped titania and its visible light decomposition of NO\(_x\). [15]. Further reports by Gole [16] and co-workers 2005 widely discussed the nature of nitrogen doped titania nanocrystals with XPS investigations. The TiO\(_2\)-N\(_x\) photocatalysts were also obtained at room temperature by employing the nitridation of anatase TiO\(_2\) nanostructures with alkyl ammonium salts. S. Livraghi [17] and co-workers investigated nitrogen-doped titanium dioxide (N-TiO\(_2\)), by a combined experimental and theoretical approach in 2006. Hexing Li et al. [18] in 2008 prepared highly active TiO\(_2\)-N\(_x\) photocatalyst by N-doping in Et\(_3\)N/ ETOH fluid under supercritical conditions. Sadhana S. Rayalu et al. [19] in 2009 synthesized N-doped mesoporous titania using templating method. Biopolymer chitosan was used as a template and also as a nitrogen source along with ammonium hydroxide. G. Cappelletti et al. [20] in 2010 prepared nano-N-TiO\(_2\) from tertiary amine. Bhekie B. Mamba et al. [21] in 2011 prepared nitrogen/palladium-co doped TiO\(_2\) photocatalysts by calcinations of the hydrolysis product of titanium isopropoxide, Ti(O\(_2\)\(_2\)\(_2\)H\(_2\))\(_4\), with aqueous ammonia.

Therefore, synthesis of N doped TiO\(_2\) can be classified into three groups: (i) sputtering and implantation techniques, i.e. directly treating the target TiO\(_2\) film with high energy N-containing gas flow, (ii) high temperature sintering of TiO\(_2\) under a N containing atmosphere and (iii) sol–gel method involving the hydrolysis of Ti precursors in alcohol and water in the presence of N-precursors such as ammonia and organic amines [22]. Amongst these methods, the sol–gel method is the most successful method to synthesize N-doped TiO\(_2\) nanomaterials because of its simplicity that provides a simple method to control the nitrogen doping level and particle size, [23].

There is no well-known direct correlation between the properties of TiO\(_2\) based nanomaterials and photocatalytic activity, although the synthesis process is considered one of the most important factors controlling the reactivity of the doped TiO\(_2\) [24-28]. Contrary to the generally made assumption that the nitrogen species are the origin of visible-light photocatalysis, Ihrara et al. [29] concluded that oxygen-deficient sites are responsible whereas doped nitrogen is just inhibiting reoxidation to stoichiometric TiO\(_2\). Similarly, Martyanov et al. [30] concluded that the generated oxygen defects can successfully serve as colour centres giving rise to enhanced visible light photocatalytic activity. Recently Serpone [31] and co-workers reported that the nitrogen precursor during the modification procedure just induces formation of oxygen vacancies and colour centres, which themselves are responsible for the enhanced visible light photocatalytic activity.

N and Ti precursors are considered to be the most important factors controlling the reactivity of the doped TiO\(_2\) [32]. Several methods have been reported to synthesize visible light sensitive N-doped TiO\(_2\). However, most of the methods currently being used suffer scale-up problems, and are not environmentally friendly. For example, template methods utilize volatile organic compounds (VOCs), and high temperature treatment is required to remove the template which reduces the surface area of the synthesized materials [33]; hydrothermal or solvothermal methods involve high temperatures in an autoclave that generates corrosion and safety problems; while CVD processes are difficult to scale-up. The sol–gel method is by far the most often used method to prepare N-doped TiO\(_2\) [34,}
Using organic reagents for N-doping in this synthesis leads initially to organic residues on the nanoparticles.

In this paper, we report the preparation of N-doped titania nanoparticles by sol-gel process using titanium isopropoxide and amine. We also report their chemical compositions, structures, optical properties and photocatalytic activities. The photoactivity of N-doped TiO$_2$ may vary with preparation method, precursors used to dope nitrogen, target pollutant, and the intensity of the light used for photocatalysis. We pay special attention to the precursors used for nitrogen doping, because they may have determinative effect on the physico-chemical properties of N-doped TiO$_2$. We found that in the nitrogen-doped titania nanoparticles, the nitrogen precursor had a strong correlation with the optical response, and the photocatalytic activity. This study aims to understand the effect of different N-precursors on chemical fine-tuning and further optimization of the UV-visible light photocatalytic activity of N-doped TiO$_2$ nanoparticles through their surface chemistry. Three different nitrogen sources viz. triethylamine, diisopropylamine and triethanolamine were used in the preparation of N-doped titania nanoparticles. The properties of the prepared N-doped TiO$_2$ powders are characterized by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and diffuse reflectance spectroscopy (DRS). The relationship between the properties such as the nitrogen content measured with XPS and the photocatalytic activity with UV light are also discussed for the synthesized N-doped TiO$_2$ nanocomposites.

2. Experimental

2.1. Materials

Titanium isopropoxide was procured from Sigma- Aldrich; Propane-2-ol was obtained from Merck. Dye fluorescein was procured from Lobachemie. Triethylamine, diisopropylamine and triethanolamine were procured from Merck, Loba chemie and Oster chemical and pharmaceutical limited respectively. All materials were used as received. All the solutions were prepared with deionised water.

2.2. Synthesis of the photocatalysts

Synthesis of the TiO$_2$ nanocrystals entails the drop wise addition (1ml/min) of 30.7 ml aliquot of titanium isopropoxide in 37.6ml 2-propanol, in a 500 ml reactor with stirring for about 10 min to form a solution. To it added alkyl amine (6.61ml triethanolamine or 7ml triethylamine or 7ml diisopropylamine) with continuous stirring. 180 ml of 0.1M KOH aqueous solution was added drop wise under vigorous stirring until a transparent fluid was obtained. The wet precursor was dried in oven as a xerogel at 80°C overnight and subsequently calcined at 400°C for 6h under oxygen stream. The synthesized nanomaterials were named as TOL (from triethanolamine), ET (from triethylamine), DIS (from diisopropylamine) and T, the undoped titania. The commercial titania used for comparison of photoactivity was named as CT.

2.3 Photocatalytic activity of the catalysts in the aqueous phase degradation of fluoresceine

For experiments under UV light, the desired fluorescein dye solution was prepared in double distilled water. An immersion well photochemical reactor (HEBER) made of Pyrex glass was used in photocatalytic study. Irradiations were carried out using a 25W, 254nm medium pressure mercury lamp. A water circulating Pyrex glass jacket was used to eliminate IR radiation and short wavelength UV radiation. The fluorescein dye solution (10$^{-6}$ M) was poured into the Pyrex vessel of the photo reactor and aqueous dispersions of the catalyst were prepared by addition of a given weight (0.2gm) of catalyst to about 50ml of aqueous solution of the dye and sonicated it in a sonicator for 5min. The dispersion is then put in to the Pyrex vessel of the photo-reactor along with an additional amount of the dye solution (10$^{-5}$ M) just enough to fill the vessel. The dispersions were kept under constant air bubbling with the help of the air pump during irradiation. At intervals of 10 min, 10 ml aliquots of reaction mixture were withdrawn and were analysed by recording variations of intensity of fluorescence absorption band maximum in a spectrofluorometer.

The absorption vs. time plots gives the rate of decomposition of the dye. The degradation rate of
Fluorescein could be obtained by using the following relation:

$$D_e = \frac{C_t}{C_0} \times 100\%$$

where $D_e$ is the degradation rate of fluorescein after $t$ minutes of reaction, $C_t$ is the concentration of the dye after $t$ min of reaction, and $C_0$ is the initial concentration. Photocatalytic degradation of fluorescein is a pseudo-first order reaction, and its kinetics according to Langmuir-Hinshelwood kinetic model can be expressed as follows: 

$$\ln \left( \frac{C_0}{C_t} \right) = kt.$$ 

### 2.4 Characterization

X-ray diffraction patterns of the samples were recorded at room temperature with a CuKα radiation, using a Philips Analytical diffractometer and diffraction intensity was measured in the 2θ range between 20 and 90°. The average crystal sizes were determined using the Scherrer formula $D = \frac{0.9\lambda}{\beta \cos \theta}$ where $\lambda$ is the wavelength characteristic of the Cu Kα radiation, $\beta$ is the full width at half maximum (in radians) and $\theta$ is the angle at which 100 intensity peak appears.

Estimation of the content of anatase is based on the following: $X_{an} = \frac{1}{1 + 1.265I_R/I_A} \times 100\%$, where $I_A$ is the (101) peak intensity of anatase, $I_R$ is the (110) peak intensity of rutile and 1.265 is the scattering coefficient. Characterization of the surfaces was carried out using infrared spectroscopy and surface area measurements. Nitrogen adsorption isotherms were obtained for the samples with Micromeritics Tristar 3000 Surface Area and Porosity Analyzer. The surface areas were calculated using the BET equation and the mean pore size diameter was calculated using the BJH method. The adsorption edges were determined from the diffuse reflectance spectra of the samples measured using HITACHI-UV-VISIBLE u-4100 spectrophotometer. The band gap of the samples was determined by the equation $E_g = 1.239.8/\lambda$ [36], where $E_g$ the band gap energy (eV) and $\lambda$ (nm) is the wave length of the absorption edges in the spectra. SEM images of the mesoporous samples were recorded using a variable pressure Digital Scanning Electron Microscope (Model JSM – 6380 LA). TEM is recorded using a JSM -100CX, Jeol electron microscope. IR spectra were recorded with a PERKIN ELMER RXIFT -112 spectrometer. JES-FA 200 ESR Spectrometer was used for EPR measurements. For photocatalysis part the degradation of fluorescein under UV light was monitored by absorbing the intensities of residual fluorescein with HITACHI FL 2500 spectrofluorometer. Raman studies were performed on Laser micro Raman System, Horiba Jobin Vyon LABRAM HR. XPS spectra were taken on ThermoScientific ESCALAB 250 instrument.

### 3. Result and discussions

The crystal phase and crystallite size of the nanomaterials calcined at 400 °C were examined by XRD (Figure 1a). This figure shows that all modified calcined nanomaterials consist of anatase crystal, although the peak intensity as well as the FWHM strongly depends on the type and amount of dopant. No distinct TiN peak is evident, indicating no phase separation, and the dopant was contained in the anatase crystal structure for this composition. However, the crystallite size was found to decrease with the nature of dopant introduced into the system. All the crystallite sizes were calculated using Scherer’s equation. It can be seen that the crystal size for pure TiO$_2$ calcined at 400°C was ca. 11.3nm, whereas TOL, ET and DIS had ca. 9.1, ca. 9.8, and ca.10.4nm crystallites. The N modified nanomaterials had smaller crystallites compared to the unmodified samples, regardless of the amount of amine used. Moreover, triethanolamine reduced the crystallinity of the modified samples compared to other samples. All the prepared nanomaterials retain their mesoporosity even after calcinations at 400°C as is evident from their low angle XRD given in Figure 1b. The XRD of calcined (800°C) undoped TiO$_2$ (T) and N-doped TiO$_2$ (TOL) are given in Figure 1c.
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Figure 1. a) XRD of the samples calcined at 400°C, b) Low angle XRD of the samples calcined at 400°C; c) XRD of T and ET calcined at 800°C.

Annealing improved the crystallization of TiO$_2$ powders and accelerated the transformation from amorphous phase to anatase or rutile phase. It can be seen in the XRD pattern that anatase phase is the prevalent phase on heating up to 400°C but on calcinations to 800°C the anatase phase is converted to rutile phase. Thus the diffraction peaks of anatase TiO$_2$ corresponding to 2θ: 25.3º, 37.8º, 48º, 54º, 55° [JCPDS-84-1286] and of rutile phase to 2θ: 27.3º, 35.9º, 41.1º, 54.1º [JCPDS-86-1175] were observed. At 800°C percentage of rutile in T was 90.6% whereas in TOL it was 71.7%.

The doping reaction chemistry of titanium tetraisopropoxide with the nitrogen precursor in the hydrolysis process can be shown as follows:

$$\text{Ti (OPri)}_4 + n\text{H}_2\text{O} \rightarrow \text{Ti (O Pri)}_4 - n\text{(OH) } n + n\text{ Pri OH (n < 4)}$$

After hydrolysis, condensation polymerization of the alkoxyl oxide takes place leading to release of water as presented in the forthcoming equation:
The rate of hydrolysis in water is almost the same as we have in alcohol. Only mark able difference is that the hydrolysis rate in alcohol is much slower than in water, due to the fact that water is a stronger acid with stronger nucleophilic attacking ability than that of alcohol. In the presence of triethanolamine, similar reaction of aminolysis will occur as follows:

\[
\text{N(CH}_2\text{CH}_2\text{OH})_2+\text{Ti(OPr)}_4\rightarrow\text{N(CH}_2\text{CH}_2\text{OH})_2\rightarrow\text{Ti(OPr)}_4\rightarrow\text{N(CH}_2\text{CH}_2\text{OH})_2\text{N(OPr)}_3\text{Ti}\rightarrow\text{Ti(OPr)}_3\text{N(CH}_2\text{CH}_2\text{OH})_2+\text{Pr}^i
\]

Hence overall reaction will be:

\[
\text{Ti(OPr)}_4+n\text{N(CH}_2\text{CH}_2\text{OH})_2\rightarrow\text{Ti(OPr)}_4+n\text{N(CH}_2\text{CH}_2\text{OH})_2\text{N(OPr)}_3\text{N(CH}_2\text{CH}_2\text{OH})_2+\text{Pr}^i\]

After aminolysis, due to condensation-polymerization of the alkoxoide the following reaction could occur in the precipitates by the liberation of amine as follows:

\[
2p\{\text{Ti(OPr)}_4\rightarrow\text{N(CH}_2\text{CH}_2\text{OH})_2\rightarrow\text{Ti(PrOH)}_4\rightarrow\text{N(CH}_2\text{CH}_2\text{OH})_2\rightarrow\text{Ti(PrOH)}_4\rightarrow\text{N(CH}_2\text{CH}_2\text{OH})_2\}
\]

Or

\[
3p\{\text{N(CH}_2\text{CH}_2\text{OH})_2\text{N(OPr)}_3\text{N(CH}_2\text{CH}_2\text{OH})_2\rightarrow\text{N(CH}_2\text{CH}_2\text{OH})_2\text{N(OPr)}_3\text{N(CH}_2\text{CH}_2\text{OH})_2+\text{Pr}^i\text{N(CH}_2\text{CH}_2\text{OH})_2\}
\]

The two pathways gives rise to two kinds of reaction products. The first aminolysis pathway tends to give Titania either in anatase or rutile phase, while the second one results cubic TiN structure. However in the XRD measurement only the anatase structure was observed. So we can be sure that TiN has not formed. The first mechanism is supported by the nitrogen 1s binding energy at 400.3 eV in the XPS measurement, which is close to the energy for nitrogen in a compound that contains the NH group. Bulk TiN materials should have binding energy at 397.0 eV. Thus, we can say that the nitrogen in the doped titania materials forms a complex structure with that of titanium and hydrogen in the TiO₂ lattice structure. This mechanism is also supported by the results of the FT-IR spectra of the prepared samples and the status of nitrogen in those samples is same with the results of the study by Yates and co-workers [37].

In sol-gel reaction, hydrolysis of the metal alkoxide is followed by condensation. Titanium tetraisopropoxide hydrolysis occurs through a nucleophilic substitution (SN) reaction. Therefore, when a nucleophile, e.g. water is introduced to titanium alkoxide, a rapid exothermic reaction takes place. The nucleophilic addition (AN) of water then involves a proton from the attacking nucleophile (water) being transferred to the alkoxide group and the protonated species is thereafter removed as either water or alcohol [38].

\[
\text{HOH}+\text{RO M}\rightarrow\text{MO H}+\text{ROH}
\]

The sol-gel process is a combination of hydrolysis followed by condensation reactions. Condensation involves either alcoxolation or through oxolation. In both cases an oxo bridge is formed between the metals (M–O–M). However the leaving group differs in both alcoxolation and oxolation. The factors which influence stability and energy of the overall hydrolysis and condensation processes are the electrophilicity of the metal, the strength of the entering nucleophile and the stability of the leaving group. Use of a suitable solvent may also influence the reaction kinetics because if a suitable solvent is chosen then it may be preferentially hydrolysed over the alkoxide ligands [39]. We have used polar solvent propane-2-ol in our preparation. With isopropoxide, partial hydrolysis occurs resulting in rapid hydrolysis and the formation of a precipitate [40].
Presence of acid and base catalysts also has a strong influence over reaction kinetics. In basic medium the hydroxo ligands are deprotonated thereby producing strong nucelophiles:

\[ \text{L...O...H} + \text{B} \rightarrow \text{L}^–\text{O}^– + \text{BH}^+ \]
where \( L = M \) or \( H \) and \( B = \text{OH}^– \) or \( \text{NH}_3 \)

To further verify these results, Raman analysis was performed on all the N doped samples (Figure 2a). The spectra for the samples calcined at \( 400^\circ\text{C} \) show Raman peaks at \( 144, 395, 517 \) and \( 639 \text{ cm}^{-1} \) that can be assigned to the \( \text{E}_3, \text{B}_{1g}, \text{B}_{1g}^/\text{A}_{1g} \), modes of the anatase of titania respectively, which agrees with published values [41]. However, the most intense anatase peak at \( \approx 144 \text{ cm}^{-1} \) showed significant differences amongst the different samples (Figure 2b). The Raman peaks usually display smaller line widths (FWHM) for larger crystallites due to an increase in the correlation length of the vibrations, with increasing intensity indicating greater concentrations of anatase phase. Moreover, the peaks shifted to higher frequencies, also confirming smaller crystallite sizes were formed [42].

![Figure 2a: RAMAN spectra of T, TOL, ET and DIS.](image)

![Figure 2b: Variations in the main peak at 144 cm⁻¹ of the samples T, TOL, ET, DIS.](image)
The morphology and size of the triethanolamine modified and triethylamine modified as-prepared materials were characterized by SEM analysis as shown in Figure 3a and 3b. The SEM picture shows that nanomaterials prepared from triethylamine were more compact than those produced from triethanolamine.

TEM analysis was performed to obtain more detailed information about the calcined materials (T and TOL), such as crystal size and porosity with the images given in Figure 4a and 4b. It can be seen that calcined pure TiO$_2$ are circular plates with 30 nm diameters whereas all N doped samples are plates with 100-300 nm width. Pure TiO$_2$ formed nice spherical crystals whereas in the modified system, poor crystallinity was observed. It is known that the N present in the samples retards the reorganization for forming ordered crystal structures, resulting in poor crystallinity for
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the modified systems. The TEM images also reveal that the N-doped materials were more porous. This analysis confirmed that triethanolamine had a significant effect on the morphology and the properties of the products.

To explore the crystal structure in more detail, HRTEM analysis for both the pure TiO$_2$ and the modified samples calcined at 400 °C were performed. The HRTEM micrographs for the TOL in Figure 4a demonstrate long grains having the anatase crystal phase with a d-spacing 0.35 nm. This d-spacing value is assigned to the lattice spacing of the (101) planes of the anatase phase. Upon introducing dopant into the TiO$_2$ matrix, the crystallites became smaller as was previously observed from the XRD analysis. However, the HRTEM analysis further reveals that the N doped systems (Figure 4c) have many defects (grain boundary, lattice mismatch, screw dislocation), which may be due to the presence of alkylamine in the synthesis process. Alkylamines can be selectively adsorbed on certain crystal facets of metal oxides, or form amine complexes with metal alkoxides, thus leading to orientated growth or aggregation of the metal oxide particles.
To compare the source materials, triethanolamine, triethylamine and diisopropylamine, were used at the same concentration to prepare N-doped TiO₂. The UV–Vis diffuse reflectance spectra of the powder are shown in Figure 5. A higher absorbance was obtained with triethanolamine than the other two, indicating a higher amount of nitrogen was doped with triethanolamine. This absorption in visible region was caused by N-doping as has been reported in literature. The band gap values for these nanomaterials were found to be ca. 3.2 eV for T, ca. 3.04 eV for DIS, 2.94 eV for ET and finally 2.90 eV for TOL.

Figure 6a shows a typical XPS spectrum for the N doped TiO₂ nanomaterial TOL synthesized by the sol–gel process. XPS peaks show that the TiO₂-N powder contains Ti, O, N, and C elements. The presence of carbon is ascribed to the residual carbon from the precursor solution, and any adventitious hydrocarbon from the XPS
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According to mumur of the TiO₂ crystal lattice, or were adsorbed onto the surface of the crystals. For further analysis of the chemical structure of the investigated TiO₂ samples, five areas of the XPS spectrum: for the Ti 2p around 460 eV, the N 1s around 400 eV, the O 1s around 530 eV and the C 1s around 286 eV region were examined. When scanning the Ti 2p regions, significant differences are observed at the binding energies between the pure TiO₂ and the modified system (Figure 6b). According to Gilindo et al., TiO₂ Ti 2p3/2 showed peaks at the binding energies 458.8 eV [43]. This XPS analysis revealed that the binding energy for Ti 2p3/2 shifted to lower values compared to pure TiO₂. The small shift of binding energy of the Ti 2p3/2 peak is attributed to the change of the valence state of Ti⁴⁺. The O1s XPS spectra also shows significant changes upon N incorporation, with the peak shifted to a lower binding energy than the pure oxygen peak in TiO₂ (Figure 6c). The binding energy for O in TiO₂ is 530 eV; whereas it is 529.92 eV for N doped TiO₂. The most interesting changes occur around the C 1s peak, and the resolved C peak shows that three different types of carbon containing groups are present around 288, 286, and 284 eV, representing the O-C=O, C-N and C-C & C-H groups, respectively. However, only two instead of three carbon groups such as O-C=O and C-C & C-H were present in the pure TiO₂ system. This additional carbon peak indicates that the amine group is directly absorbed onto the surface of the materials, forming metal complexes. It is well known that with two nonbonding electrons of nitrogen can act as a Lewis base and forms complexes with electrophilic metal ions [44].

N1s XPS peak with a core level binding energy of 400.3 eV was observed for the three kinds of N-doped TiO₂ samples (Figure 6d). The analysis of the binding energy of N 1s for the N-doped materials showed that two types of N are present in the as-prepared nanomaterials. An intense peak centred at 400.3 eV and a small peak centred at 399.4 eV, assigned for chemisorbed and interstitial N, respectively [45, 46]. However, the binding energies are greater than the typical binding energy of 397.2 eV in TiN [47]. This higher energy shift can be attributed to the 1s electron binding energy of the N atom in the environment of O-Ti-N. When nitrogen substitutes for the oxygen in the initial O-Ti-O structure, the electron density around N is reduced, compared to that in a TiN crystal, because of the O atom bonded to the Ti atom.

Recently, most of the studies regarding the N doped TiO₂ systems have performed XPS analysis to investigate the chemical state of N. Chen and Burda found that the signal at 401.3 eV is attributed to O–Ti–N, based on the redox chemistry involved [48]. In another study, Yang et al. [49] reported a binding energy of 400.1 eV which was assigned to hyponitrite at the surface. Thus, the nitrogen state in the doped TiO₂ may vary from case to case. However, very recently Huo et al. [18] reported a peak at 399.6 eV, ascribed to the N species incorporation into the titania matrix. Keeping all this in mind, it can be concluded that all N species were incorporated into the TiO₂ matrix and the resultant nanomaterials were described as N doped TiO₂.

ESR measurements were performed at room temperature in air. Figure 7 displays the ESR spectra of three kinds of N-doped TiO₂ samples TOL, ET and DIS. No ESR signals were observed for precursors of Ti and commercial TiO₂, indicating that they are free of paramagnetic species. However, after heat-treatment at 400 °C in air for 4 h, resultant N-doped TiO₂ showed ESR signal with g = 2.004, due to the formation of SETOV [50]. This indicates that as-prepared novel-TiO₂ has intrinsic solid defects (i.e. single-electron-trapped oxygen vacancy denoted as SETOV, i.e., F⁺ color centres) as compared with undoped titania as well as commercial titania. The three kinds of N-doped TiO₂ samples showed a triplet ESR signal with g values of 1.985, 2.004, and 2.019. No characteristic ESR signal of Ti³⁺ (g = 1.96) ion was detected, well corresponding to the absence of Ti³⁺ species in relevant XPS analysis.

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Figure 6a: XPS survey of TOL.

Figure 6b: XPS peak of Ti 2p3/2.

Figure 6c: XPS peak of O1s.
Figure 8 shows the PL spectra of undoped and nitrogen doped TiO$_2$. The sample quantity used for the measurement was the same (50 mg), and the samples were excited at a wavelength of 300 nm. The spectrum at 561 nm is emission signal originating from the charge transfer transition from an oxygen vacancy trapped electron [51]. Interestingly, the intensities of PL spectra for N-doped TiO$_2$ catalysts show a significant decrease. A trend in the peak intensity has been observed in the following order: T $>$ ET $>$ DIS $>$ TOL. Because the PL emission is the result of radiative recombination of excited electrons and holes, the lower PL intensity of the N-doped sample clearly implies decreased recombination of excited electrons and holes in the N-doped TiO$_2$. So the TOL has the enhanced photocatalytic activity, it is confirmed by photocatalysis experiments.
Lakshminarasimhan et al. [52] prepared three-dimensional and thermally stable mesoporous TiO$_2$ without the use of any surfactants. The surface area and pore volume of the calcined materials were characterized by nitrogen adsorption studies, which were summarized in Table 1. Figure 9 shows a typical nitrogen adsorption isotherm for calcined TOL, which exhibits an H2 hysteresis loop, typical for mesoporous materials. The pore volume for all samples follows a clear trend. For example, pure TiO$_2$ possessed a 0.083 cm$^3$/g pore volume while triethanolamine increased the pore volume to 0.415 cm$^3$/g. However, with triethylamine and diisopropylamine the pore volume significantly decreased than that of TOL. The BET surface areas of the calcined materials given in Table 1 demonstrate that the sample TOL possessed higher surface areas compared to the pure TiO$_2$, ET and DIS. This is expected as the SEM and TEM analysis demonstrated that denser materials were formed using a triethylamine. The origin of this effect likely comes from the hydrolysis and condensation pathways in the sol-gel process. The pure metal alkoxide with the required amount of KOH was prepared in basic condition. While hydrolysis kinetics is retarded in basic conditions, the condensation kinetics of metal alkoxides is enhanced. Therefore, base-catalysed condensation (and hydrolysis) should be directed toward the middle rather than the end of chains, resulting in the formation of compact, highly branched species [53] having lower surface areas. In an acidic medium, the hydrolysis reaction is accelerated. The acid converts negatively charged alkoxide groups into better leaving groups by protonating them. Because of this, acid catalysed condensation occurs at the end of chains rather than the middle, resulting in longer polymer chains with little branching and high surface areas. Upon introducing triethanolamine into the synthesis process, the pH of the solution increases. Hence, the hydrolysis rate is decelerated and the condensation kinetics is accelerated upon increasing the pH of the solution. The condensation is then directed towards the middle, instead of the ends of the chain. The acidity of triethanolamine is highest and that of triethylamine is lowest thus reaction with triethanol amine is least basic (table 2) and most acidic resulting in the formation longer polymer chains with surface areas. Moreover, triethanolamine with a lone pair of electrons acts as a basic catalyst. Hence, in higher pH of triethanolamine, more compact materials are produced leading to decrease in surface area.
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Figure 9: Surface area and pore volume of TOL.

Table 1: BET surface areas of T, TOL, DIS and ET

<table>
<thead>
<tr>
<th></th>
<th>BET surface area</th>
<th>Pore volume</th>
<th>Pore size</th>
<th>doping amount of N (atom %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure titania</td>
<td>33</td>
<td>0.083</td>
<td>26</td>
<td>-</td>
</tr>
<tr>
<td>Triethanolamine</td>
<td>53</td>
<td>0.415</td>
<td>10.7</td>
<td>0.4</td>
</tr>
<tr>
<td>Diisopropylamine</td>
<td>41</td>
<td>0.253</td>
<td>23</td>
<td>-</td>
</tr>
<tr>
<td>Triethylamine</td>
<td>50</td>
<td>0.338</td>
<td>19.9</td>
<td>0.4</td>
</tr>
</tbody>
</table>

Table 2: Physical properties of triethanol amine, diisopropyl amine and triethyl amine

<table>
<thead>
<tr>
<th></th>
<th>Triethanolamine</th>
<th>Diisopropylamine</th>
<th>Triethylamine</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular formula</td>
<td>C$<em>6$H$</em>{15}$NO$_3$</td>
<td>C$<em>6$H$</em>{15}$N</td>
<td>C$<em>6$H$</em>{15}$N</td>
</tr>
<tr>
<td>Molar mass</td>
<td>149.188 g/mol</td>
<td>101.19 g mol$^{-1}$</td>
<td>101.19 g mol$^{-1}$</td>
</tr>
<tr>
<td>Appearance</td>
<td>pale yellow liquid</td>
<td>Colourless liquid</td>
<td>Colourless liquid</td>
</tr>
<tr>
<td>Density</td>
<td>1.126 g/cm$^3$</td>
<td>0.717 g/mL liquid</td>
<td>0.7255 g/cm$^3$</td>
</tr>
<tr>
<td>Melting point</td>
<td>20.5 °C</td>
<td>-61 °C</td>
<td>-114.7 °C</td>
</tr>
<tr>
<td>Boiling point</td>
<td>335.4 °C</td>
<td>84 °C</td>
<td>88.7 °C</td>
</tr>
<tr>
<td>Solubility in water</td>
<td>Miscible</td>
<td>Miscible</td>
<td>Miscible</td>
</tr>
<tr>
<td>pKa</td>
<td>7.8</td>
<td>11.05</td>
<td>10.78</td>
</tr>
</tbody>
</table>
Environmental pollution due to the release of chemicals from industrial sectors has been a major concern in recent times. The major constituents of the pollutants are the dyes used in textile industry, food industry, ladder industry etc. Many efforts have been suggested to mitigate the serious environmental contamination problem. Photocatalytic degradation of dyes is one of them. So photo degradation of fluorescein was used as a probe reaction to test the photocatalytic activity of prepared N-doped catalysts (Figure 10). The photocatalytic activity of all catalysts was evaluated by measuring the absorbance (A) of the dye fluorescein’s fluorescence spectrum at 518.5 nm during every 10 min interval. With the assumption that Beer’s law was obeyed, the graph of $A_t/A_0$ against $t$ (where $A_0$ is the intensity of the dye peak at 518.5 nm after stirring in the dark) is equivalent to the graph of $C_t/C_0$ against $t$ and the latter was plotted as shown in Figure 9. It can be seen that all N-doped titania outperformed the undoped titania in the degradation of fluorescein. It can also be seen that TOL is more effective in photodegradation. Knowing that TOL has band gap ca. 2.90 eV we can say that it can act as a better photocatalyst in this case. The increase in photoactivity of synthesized N-doped photocatalysts must be due to incorporation of nitrogen in titania. That led to several modifications in physical properties such as band gap, thermal stability, particle size and photoluminescence properties. It is widely accepted that the formation of SETOV in TiO$_2$ matrix results in enhanced absorption of radiation [54, 55]. Considering that the intensity of the triplet ESR signal of N-doped TiO$_2$ samples is directly proportional to the concentration of SETOV, we can say that TOL having highest intensity in the ESR signal had highest SETOV and hence showed highest photocatalytic properties.

The high surface area of TOL is also one of the possible reasons of TOL showing highest photocatalytic activity. The photocatalytic efficiency of a TiO$_2$ photocatalyst depends not only on the electronic properties of the materials. The availability of active sites on the material surface also plays a major role in the ability of the photocatalytic material to degrade organic contaminants. A photocatalyst can produce an infinite amount of oxidising species to no effect unless the resulting radicals migrate to the TiO$_2$ surface where they can initiate the oxidation of the organic species from the surrounding environment. Therefore, properties such as crystal size and structure, pore size/volume, density of OH groups, surface charge, number and nature of trap sites and absorption/desorption characteristics all play an important factor in the photocatalytic activity of synthesized TiO$_2$ photocatalysts. Generally large surface areas will result in an increase in the number of active degradation sites available for degradation.
reactions. Surface hydroxyl groups participate in the photocatalytic process in a number of ways. They trap photoexcited electrons and produce OH• radicals and they can also act as active absorption sites for pollutants. Higher the surface area higher will be surface hydroxyl groups. Because ET and Dis are produced with lower surface than TOL they possess fewer surface hydroxyl groups and as such this is considered as one of the reasons why ET and DIS are weaker photocatalyst than TOL.

4. Conclusion
Triethanolamine, diisopropylamine and triethylamine were separately used as precursors to prepare N-doped samples by base catalysed sol-gel process. The photocatalytic activity of all the synthesized nanomaterials was compared by monitoring the photo degradation of fluorescein dye under UV-light. It was found that triethanolamine possessed highest photocatalytic activity. Doped-N played a role in separating photo generated e−–h+, contributing to high photocatalytic activity. Photocatalytic activity of N-doped TiO2 samples were attributed to the formation of SETOV. This might account for the different photocatalytic performance of “TOL, ET and DIS”, N-doped TiO2 samples. In view of the exclusive characteristics of triethanolamine, it should be pronounced that triethanolamine is one of the most promising precursors for designing N-doped photocatalyst.

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