



Synthesis and Characterization of Visible-Light Active Nitrogen-Doped TiO₂ Photocatalyst

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Nitrogen-doped titania (N-doped TiO₂) has been synthesized through the hydrolysis of N-substituted titanium isopropoxide precursors followed by annealing treatment in air at desired temperatures. The resulting N-doped TiO₂ were characterized using TGA, XRD, BET, XPS, TEM and UV-VIS spectrophotometer. The XRD result showed that the structure of N-doped TiO₂ was anatase. The crystallite size of N-doped TiO₂ increased with the increase of N/Ti proportion. The pore properties were investigated from nitrogen gas sorption analyzer, showing a mesoporous structure of its N-doped TiO₂ with a high specific surface area and a sharp pore radius distribution. The substitution of oxygen sites with nitrogen atoms in the TiO₂ structure was confirmed by X-ray photoemission spectroscopy (XPS). The doping of nitrogen could extend the absorption edge into the visible-light region led to a clear decrease in the band gap on N-doped TiO₂ (compared to pure titania and Degussa P25). The adsorption capacity and adsorption equilibrium constant were also improved by the doping of nitrogen. Catalytic application on methylene blue photodegradation under visible-light irradiation indicated that N-doped TiO₂ provide better activity comparing to the pure ones.

Key Words: Photocatalyst, Nanosize, Optical absorption.

INTRODUCTION

Photocatalysis has been thought to be a fascinating approach for resolving the embarrasments of energy, environment and resource for several decades^{1,2}. Anatase type TiO₂ semiconductor is very often used photocatalyst for water purification and other environmental problem solutions because of its stability, nontoxicity, a relatively satisfied activity, low cost, high oxidation potential and chemically favourable properties³. However, anatase has a high energy of the band gap ($E_g > 3.2$ eV) and therefore could be excited by UV radiation only ($\lambda < 380$ nm). Therefore, developing a modified visible-light sensitive TiO₂ photocatalyst plays an important role in increasing the utilization rate of solar energy and promoting the application of photocatalysis technology and is the most important and challenging research subject in the photocatalysis field⁴.

Early attempts for shifting of TiO₂ absorption into visible-light region mainly focus on the transition metals doping^{5,6} but shortcomings of metal doped TiO₂ such as thermally instability, its tendency to form charge carrier recombination centers⁷, as well as the expensive ion implantation facilities make metal-doped TiO₂ impractical⁸. Recently, nonmetal-ion-doping has been proposed to be an efficient method for preparation of modified TiO₂.^{9,10} Asahi *et al*.⁹ were successfully

intrigued the interest in the anion doping (such as N, C, S, P and F) of TiO₂. Among these anion dopants, nitrogen seems to be the most effective dopant due to its similar size to oxygen and small ionization energy¹⁰. Therefore, nitrogen doped TiO₂ becomes the most studied material relating to its synthesis, characterization and application.

N-doped TiO₂ has been prepared by hydrolytic process¹¹, mechanochemical technique¹², reactive DC magnetron sputtering^{13,14}, solvothermal process¹⁵, high temperature treatment of TiO₂ under nitrogen atmosphere^{9,16} and sol gel method^{17,18}. However, all these processes either required a special apparatus for synthesis or require tight control of experimental conditions. It seems that the sol gel method is the most successful method to prepare N-doped TiO₂ nanoparticles, because it affords simplicity in controlling the nitrogen doping level and particle size by simple variations in experimental condition, such as hydrolysis rate, pH of the solution and solvent systems¹⁷.

In this paper, we report a one step simple sol gel method to synthesize nanometer-sized visible-light N-doped TiO₂ photocatalyst through the hydrolysis of N-substituted titanium isopropoxide precursors. The elemental nitrogen was derived from dodecylamine. The photocatalytic activity of resulted material was estimated in the system of aqueous solution of methylene blue under visible-light, respectively. The contribution of nitrogen doping into titania to the adsorption

characteristic and the kinetic constant of photocatalytic oxidation of methylene blue in aqueous suspension were investigated. The effect of N/Ti proportion on the photocatalytic activity was also studied.

EXPERIMENTAL

Synthesis of N-doped TiO₂: The N-doped titania catalyst were prepared as follows: a mixture of 3 mL of Ti(OPr)₄, 4.7 mL dodecylamine and 80 mL of absolute ethanol was mixed and refluxed for 4 h at 70 °C to provide a clear solution. This precursor solution was then cooled to room temperature, which then added glacial acetic acid to control the pH. Hydrolysis process was then achieved by adding 14 mL of distilled water. The resulting yellowish precipitate was centrifuged and washed subsequently with distilled water and ethanol. Finally, the N-doped TiO₂ were vacuum-dried and calcined at a heating rate of 2 °C/min in air atmosphere for 4 h at 450 °C, obtaining N-doped TiO₂ nanocrystalline (denote as TN1). A series of N-doped TiO₂ were prepared by varying of dodecylamine volume (corresponding to N/Ti proportion of 0, 2, 4, 6 and 8 mol %) to obtain pure titania, TN2; TN3, TN4 and TN5, respectively.

Characterization: The N-doped TiO₂ powder was analyzed by thermogravimetric analysis with a Perkin Elmer, diamond-thermogravimetric analysis instrument using a 10 °C/min ramp up to 800 °C. The crystal structure of the products was examined with X-ray powder diffractometer (Shimadzu, X-6000) with Cu K α radiation ($\lambda = 0.15406$ nm). The specific surface area of catalysts was measured by standard BET apparatus (quantachrome autosorb-2) and the pore size distribution of the catalysts was determined by the Barrett-Joyner-Halenda (BJH) method. UV-visible diffuse reflectance spectra were obtained for the dry-pressed disc samples using a UV-visible spectrophotometer (UV-2450, Shimadzu) to determine the absorption edge of catalysts. The elemental analysis was done by X-ray Photoelectron spectroscopy analysis (thermo-advantage 5200W).

Adsorption test: The adsorption behaviour of N-doped TiO₂ were determined by testing resulted material adsorption in the dark as follow: 0.1 g of prepared catalyst powders were poured into 10 mL of methylene blue solutions with different initial concentrations and put into a shaker to achieve the equilibrium for 24 h. The methylene blue concentration in the N-doped TiO₂ suspensions before and after the adsorption tests were analyzed to determined the amount of methylene blue on the catalysts.

Photodegradation of methylene blue: The photocatalytic activity of the N-doped TiO₂ was determined by measuring the decomposition of methylene blue under visible-light. A 150 W high-pressure xenon arc lamp was used as the visible-light source, respectively. The initial concentration of methylene blue was 1×10^{-5} M. The methylene blue was centrifuged and the concentration determined with a spectrophotometer by measuring the absorbance at 663.5 nm, respectively.

RESULTS AND DISCUSSION

N-Doped TiO₂ can be prepared in several ways. In this research we synthesized N-doped TiO₂ through sol gel method

by hydrolysis of N-substituted titanium isopropoxide precursors in alcohol solution. We found that complexation of organic amines on the Ti metal center creates highly efficient precursors N-doped TiO₂ nanoparticles. Advantages of this route are simple method, high doping levels, controllable structure and high surface area at low cost. In the synthesis the nitrogen has been doped into the lattice and/or attached to the nanoparticle's surface. However, at the same time, there is water and organic residue adsorbed on the surface and enclosed into the amorphous and porous N-doped TiO₂ powder.

The crystal structure of a photocatalyst is an important property for catalytic activity of the nanoparticles. The crystal structures of the synthesized N-doped TiO₂ were studied by X-ray powder diffraction (Fig. 1) which indicated that all catalysts have the pure anatase phase. There are no specific peak of Ti-N or N-O was detected in the XRD spectra. The crystallite size were measured using the Debye-Scherrer¹⁸ formula, resulting the size of 7.08, 8.8, 10.1, 11.6, 13.2 and 14.7 nm for the pure titania, TN1, TN2, TN3, TN4 and TN5. It showed that nitrogen doping provide an increased of crystallite size, which due to the higher radius of a nitrogen atom (70 pm) than oxygen (66 pm). As a consequence, the existence of N in the titania lattice leads to an enlargement of the crystallite size.

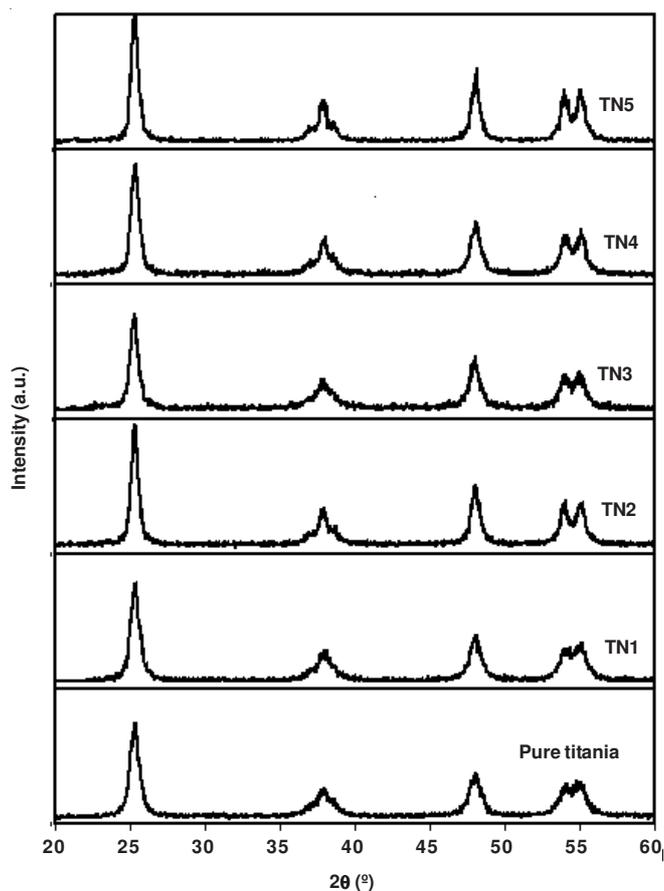


Fig. 1. XRD patterns of prepared TiO₂ catalyst

The thermogravimetric analysis (TGA) was done to study the thermal behaviour of the N-doped TiO₂ compare to the pure titania. Fig. 2 showed thermogravimetric analysis curves

of the pure titania and N-doped ones (TN2). The total weight loss in the whole temperature range was ~17 % for pure titania and ~19 % for TN2. The higher total lost weight of N-doped TiO₂ than the pure TiO₂ was due to releasing of dodecylamine as nitrogen source. The thermogravimetric analysis result of pure titania (Fig. 2) was only assign the released of water and solvent. While, the thermogravimetric analysis curve of the N-doped TiO₂ showed that there is about 10 % of weight loss from room temperature up to 220 °C, which is mostly due to the loss of physically adsorbed or embedded water and solvent on the surface of the N-doped TiO₂. From 220 to 400 °C, there is about 7 % weight loss of the N-doped TiO₂ sample related to the release of dodecylamine. From 400 to 500 °C there is much slower (about 1 %) weight loss of the N-doped TiO₂ sample in association with the crystallization of these nanoparticles, as confirmed by XRD. Above 500 °C, there is very little, about 1% weight loss of the N-doped TiO₂ due to the released of chemisorbed water. Annealing temperature of 450 °C was chosen based on thermogravimetric analysis data that the surfactant will be released by calcinations above 400 °C, but there still nitrogen left in the TiO₂.

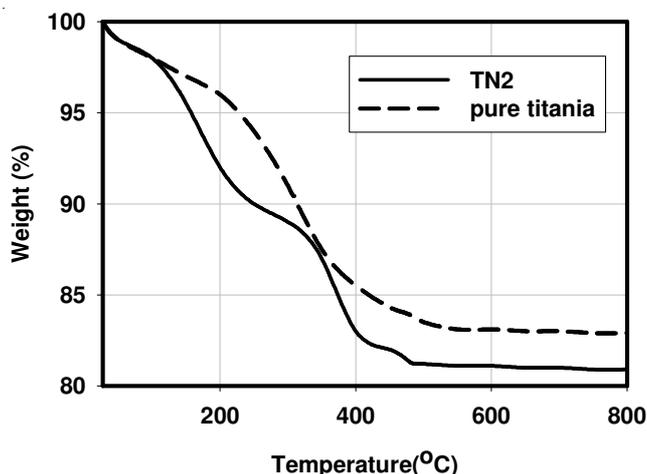


Fig. 2. TGA curve of nitrogen-doped TiO₂ (TN2) and pure TiO₂

A nitrogen adsorption/desorption tests have been done to investigate the effects of the nitrogen doping on porosity of catalysts and their isotherms curves were presented in Fig. 3. It could be seen that the isotherms of all prepared titania catalyst showed a hysteresis loop of type IV¹, which indicated that all titania prepared by sol gel method developed in this research had mesoporous structure. It also indicated in Fig. 3 that the volume adsorbed on N-doped TiO₂ was higher than that of the pure titania at the same relative pressure.

The result of pore size distribution analytical as shown in Fig. 4 obviously showed that all synthesized titania had a

mesoporous structure. The specific surface area, average pore diameter and total pore volume of the samples were measured by the BET method. The analytical results (Table-1) showed that there is an optimum of N/Ti proportion for resulting a high specific surface area and total pore volume of N-doped TiO₂. The results also showed that the pore size of all samples were similar in the range of 1-10 nm. The N-doped TiO₂ had larger pore size than the pure ones, which generally at higher concentration of N/Ti proportion raised the average pore diameter.

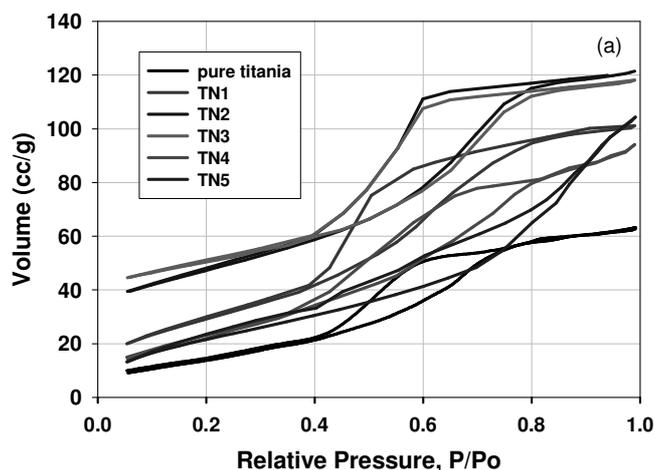


Fig. 3. Nitrogen adsorption-desorption isotherms of prepared TiO₂ catalyst

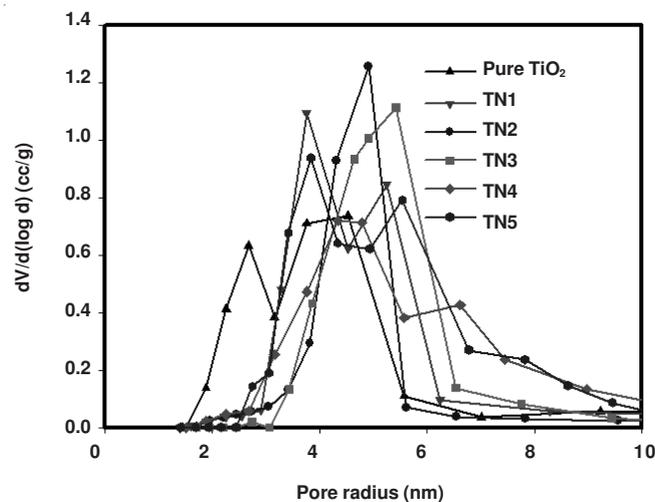


Fig. 4. Pore size distribution of prepared TiO₂ catalyst

TEM analysis was performed to examine the size and shape of N-doped TiO₂ (TN2), as shown in Fig. 5, which is indicated the crystalline nature of N-doped TiO₂ spheres. High resolution lattice image shown in Fig. 5d confirmed that the

TABLE-1
CRYSTAL SIZE AND BET DATA OF PREPARED TiO₂ CATALYST

	Pure TiO ₂	TN1	TN2	TN3	TN4	TN5
Band gap energy (eV)	3.02	2.88	2.8	2.85	2.78	2.76
Crystal size (nm)	7.08	8.8	10.1	11.6	13.2	14.7
BET surface area (m ² g ⁻¹)	56.73	110.9	167.4	177.4	89.6	84.68
Average pore diameter (nm)	4.48	5.1	5.6	5.3	6.5	7.5
Total pore volume (cm ³ g ⁻¹)	0.098	0.156	0.232	0.206	0.177	0.161

sample comprised of connected crystalline titania nanoparticles which corresponds to (101) interplanar spacing of anatase TiO₂ phase consistent with the XRD data. The TN2 powder possessed -10 nm crystallite, which is also consistent with that calculated from the XRD data.

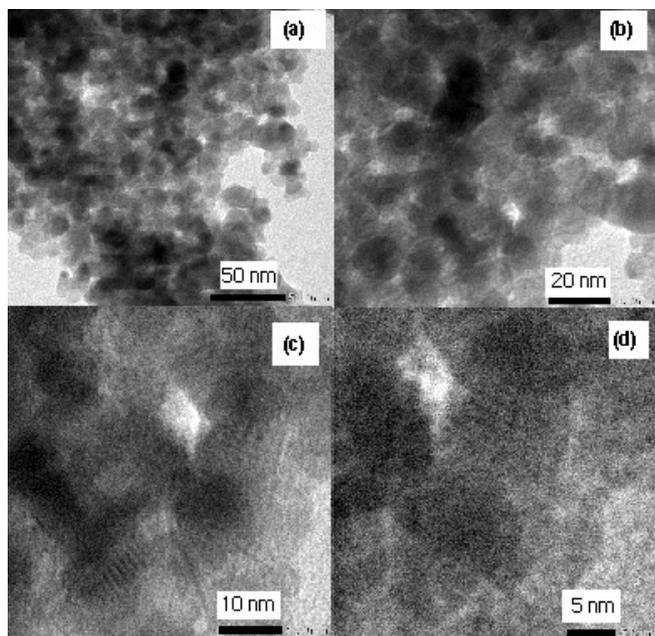


Fig. 5. TEM images of nitrogen-doped TiO₂ catalyst (TN2)

To evaluate the electronic environment and state of the nitrogen atom in TiO₂ network, XPS studies have been carried out. The nitrogen 1s core level of N-doped TiO₂ shows three peaks at 396.0, 398.8 and 400.5 eV, which did not found in the pure titania spectrum (Fig. 6a). Still there are a lot of controversies and debates going on for assigning the exact position of N in TiO₂. However most of researchers interpret two peaks at higher binding energies as the chemisorbed γ N₂ or molecularly adsorbed nitrogen species, whereas the peak at 396 eV was assigned to the atomic substitutionally bound N⁻ species in the TiO₂ lattice³. Irie *et al.*^{16,19} and Diwald *et al.*^{20,21} reported that the peak at 396 eV in the XPS spectra was attributed to a chemically bound N⁻ species within the crystalline TiO₂ lattice. Most N⁻ species in the N-TiO₂ existed in the form of nitrides such as N in the O-Ti-N linkage, corresponding to the binding energy (BE) of 399.4 eV, while only small amounts of N were present in form of surface adsorbed ammonia, with the BE located at 396.0 eV. Gopinath²² strongly commented his view and concluded that the peak corresponding to 396-397 eV is due to the substitutional N doping. Similarly Nakamura *et al.*²³, Yates *et al.*²⁴ and Parida *et al.*²⁵ assigned their 396 eV peak to substitutional atomic β N doping. Considering all above references one fact is clear that the peak around 396 eV is for atomic substitution of N by replacing the O atom in TiO₂ lattice and the peaks on 398.8 and 400.5 eV are for chemisorbed λ N₂ and surface adsorbed NH_x or NO_x species.

In the Ti 2p XPS spectra (Fig. 6), there is significant decrease in binding energy of Ti2p^{3/2} on N-doped TiO₂ (458.6 eV for TN2 and 458.4 eV for TN3) compared to pure titania (459 eV), which again confirmed the nitrogen incorporation in to titania matrix. The Ti 2p BE curve of TN2 and TN3 also

showed an intermediate peak centered at *ca.* 457.5 eV, which correspond to Ti-N bound. By introducing negatively charge N in to the matrix, the binding energy of Ti can be significantly lowered. The atomic content of nitrogen in N-doped TiO₂ mesoporous spheres was calculated from XPS data, which was found to be 2.1, 3.6, 3.9, 4.4 and 4.8 atomic % for TN1, TN2, TN3, TN4 and TN3 respectively. It obviously showed that the higher N/Ti proportion provide a higher concentration of nitrogen doped.

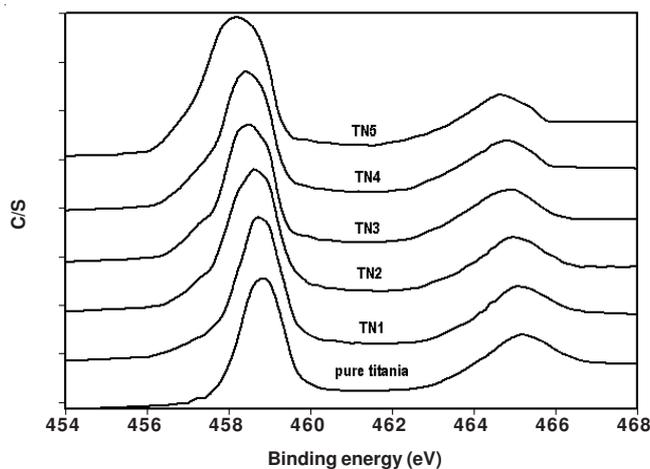
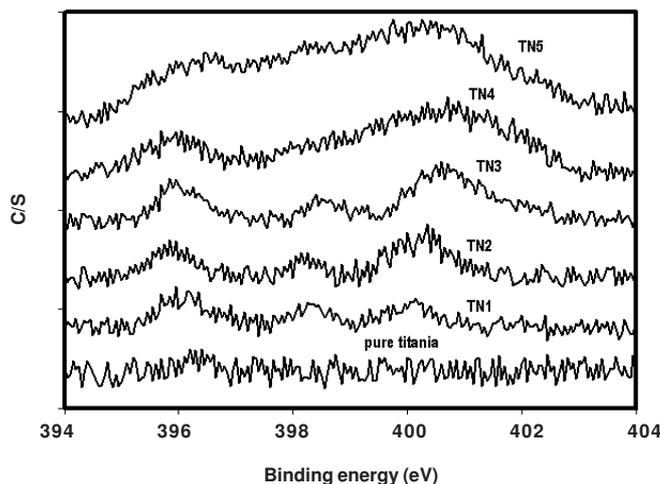


Fig. 6. XPS spectra of different TiO₂ catalyst: N1s (up) and Ti2p (down)

The optical absorbance and reflectance was used to study the capability of nitrogen doping to photosensitize the TiO₂ nanoparticles. The absorbance shift of the N-doped TiO₂ can be observed from the reflectance spectra of undoped TiO₂ (Degussa P25 and pure) and N-doped TiO₂ as shown in Fig. 7. The yellowish N-doped TiO₂ sphere powders show good absorbance of visible-light. It can be seen from Fig. 7 that the visible-light absorption is high and extended up to 550 nm in the case of N-doped TiO₂ calcined at 450 °C compared to that of undoped TiO₂. It may be due to that nitrogen species occupy some of the oxygen positions in the lattice. This also rules out the occupancy of N in any other positions such as interstitial sites, which should give rise to a mid gap band/level between valence and conduction bands. The band gaps of N-doped TiO₂ were calculated by the equation²⁶.

$$E_g = 1239.8/\lambda$$

where E_g is the band gap (eV) and λ (nm) is the wavelength of the absorption edges in the spectrum. The band gap for prepared of N-doped TiO₂ as calculated from the absorption edge in the visible region was also listed in Tabel-1. This result is in agreement with those reported by Asahi *et al.*⁹ that the optical absorption edge of N-doped TiO₂ shifted to the visible-light region and proved that mixing the N 2p and O 2p states narrowed the band gap.

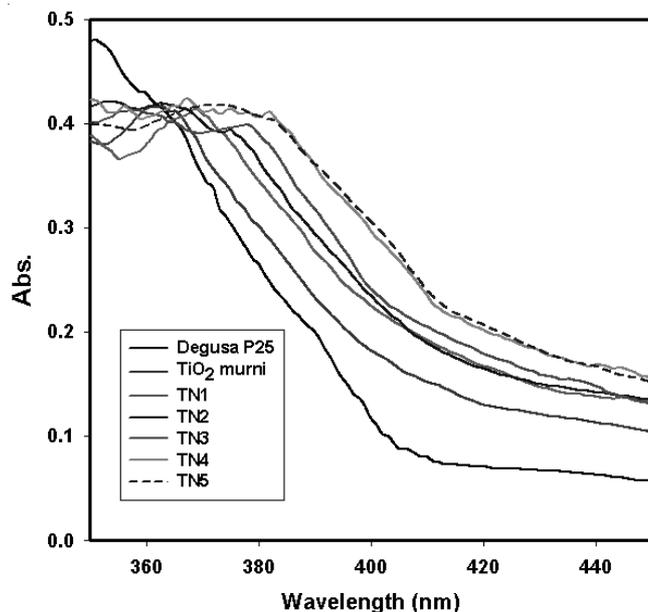


Fig. 7. UV VIS absorption spectra of prepared TiO₂ catalyst compared to Degussa P25

Photocatalytic activity: The adsorption properties of prepared catalyst has been studied as saturated adsorption capacity (Γ_{max}) and adsorption equilibrium constant (K_a) which determined by dark adsorption test of methylene blue. Following is Langmuir adsorption model²⁷, The values of Γ_{max} and K_a were obtained from the C_e/Γ versus C_e (Fig. 8) and the fitting listed in Table-2.

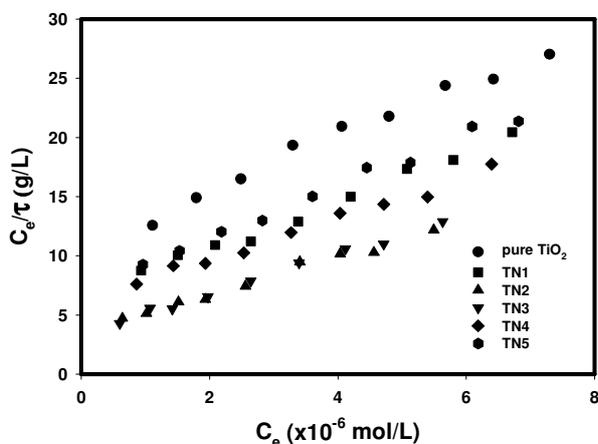


Fig. 8. The adsorption isotherm of MB on prepared TiO₂

The result showed that the saturated adsorption capacity (Γ_{max}) of the nitrogen-doped TiO₂ were higher than the pure TiO₂. The result also indicated that the nitrogen doping on

TABLE-2
ADSORPTION ISOTHERM DATA OF PREPARED TiO₂
CATALYST IN METHYLENE BLUE SYSTEM

Catalyst	Saturated adsorption capacity, Γ_{max} (10^{-6} mol g ⁻¹)	Adsorption equilibrium constant, K_a (L mol ⁻¹)	R ²
Pure titania	4.39	20867.89	0.9833
TN1	4.95	30832.51	0.9892
TN2	6.42	47897.97	0.9865
TN3	5.92	49860.05	0.9875
TN4	5.73	28189.3	0.9923
TN5	4.63	29968.35	0.9916

TiO₂ lead to the increased of adsorption equilibrium constant (K_a). It seems that the change of physical properties such as specific surface area, porosity and total pore volume, have influenced the adsorption properties of the catalyst. The catalyst, which have higher specific surface area have a better adsorption capacity and adsorption constant (TN2 and TN3).

The photocatalytic activity of prepared TiO₂ catalyst samples have been studied by measuring the decomposition of aqueous solution of methylene blue under visible-light with initial concentration 10^{-5} mol/L. The experimental result of the photocatalytic test was shown in Fig. 9, which demonstrated that all nitrogen-doped TiO₂ catalyst achieved significantly photodegradation of methylene blue than the pure TiO₂. It also showed that the catalyst with higher saturated adsorption capacity and adsorption equilibrium constant were having better activity as methylene blue photodegradation catalyst. That's mean that the adsorption process played an important part of the photocatalytic process in the catalyst. Therefore, the Langmuir-Hinshelwood (L-H) kinetic equation is being an appropriate model to describe this kind of reaction.

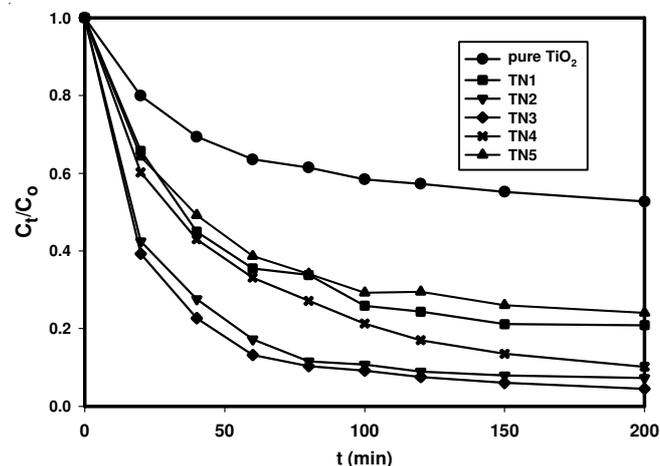


Fig. 9 Photodegradation of methylene blue under visible-light irradiation

The reaction L-H kinetics is the most commonly used kinetic expression to explain the kinetics of heterogeneous catalytic process, which can be simplified into the first order model if the substrate concentration (C) is very low. The kinetics constant (k_1) of methylene blue photodegradation using different TiO₂ catalyst could be calculated using the integrated of L-H model²⁸, which is given by:

$$r = -\frac{dC}{dt} = \frac{kK_aC}{1 + K_aC}$$

The integrated expression of this equation given by:

$$\ln\left(\frac{C_0}{C}\right) + Ka(C_0 - C) = kKa \cdot t$$

where Ka is the adsorption equilibrium constant, which already determined from adsorption test. k is the photoreaction rate constant (min^{-1}), t is the reaction time (min) and C_0 is initial concentration.

If the term $KaC \ll 1$; $r = kKaC$ and its integration to limits: $C = C_0$ at $t = 0$ and $C = C$ at $t = t$ lead L-H expression reduces to a first order kinetics and formulated as follow:

$$-\ln \frac{C}{C_0} = k_1 t$$

where k_1 is the apparent rate constant (min^{-1}) and $k_1 = kKa$. The kinetic parameters (k_1 and k) were obtained from the fitting

of $\ln \frac{C}{C_0}$ vs. t plot and the result listed in Table-3.

TABLE-3
KINETICS DATA OF METHYLENE BLUE
PHOTODEGRADATION

Catalyst	Apparent rate constant, k_1 (min^{-1})	Ratio $k_1N\text{-TiO}_2/k_1\text{TiO}_2$	Reaction kinetic constant, k (min^{-1})	Ratio $kN\text{-TiO}_2/k\text{TiO}_2$
Pure titania	0.0063	1	0.0303	1
TN1	0.0195	3.08	0.0632	2.09
TN2	0.0346	5.35	0.0714	2.36
TN3	0.0171	5.23	0.0606	2.29
TN4	0.0331	2.70	0.0664	2
TN5	0.0158	2.50	0.0526	1.74

The kinetics data showed that all nitrogen-doped TiO_2 demonstrated better performance in the methylene blue photodegradation, which TN2 give the best performance. The apparent rate constant, k_1 , of the nitrogen-doped TiO_2 were more than three times higher compared to the pure one. Whereas the photoreaction rate constant, k , of the nitrogen-doped TiO_2 were two times higher compared to the pure one in average. TN2 have resulted the highest Ka , k_1 and k . These result indicated that the enhancement of methylene blue photodegradation in nitrogen-doped TiO_2 influenced by their larger adsorption capacity in methylene blue solution. It was obvious that the visible-light activity of nitrogen-doped TiO_2 was better than that of pure titania, which proportion of $N/Ti = 2$ (TN2) give the best performance. Furthermore, the order of methylene blue photodegradation under visible-light was not really consistent with the order of optical intensity as shown in Fig. 7 and its band gap values showed in Table-1. It is indicated that the larger surface area and higher total pore volume of nitrogen-doped TiO_2 has more contributed to higher visible-light activity than the stronger visible-light photo-absorption.

Conclusion

N-Doped TiO_2 photocatalyst has been prepared by one-step simple chemical route. The advantages of this method

over other methods of preparation are (i) use of inexpensive chemical precursors for the synthesis of N-doped TiO_2 and (ii) formation of TiO_2 as uniformly sized nanoparticles. The nitrogen-doped TiO_2 had larger crystallite size than the pure one and their crystallite size increased with the increase of N/Ti proportion. Optical absorption studies clearly identified the substitutional N-doping and localized N-states in the TiO_2 lattice. A higher photocatalytic activity for the decomposition of methylene blue in the visible region has been obtained for the N-doped TiO_2 sample compared to pure TiO_2 .

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