

SYNTHESIS, CHARACTERIZATION AND PHOTOACTIVITY EVALUATION OF NITROGEN DOPED TITANIUM DIOXIDE ON METHYLENE BLUE DYE DEGRADATION.

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ABSTRACT

Titanium dioxide has proven to be one of the most promising heterogeneous catalyst. This work explores the photocatalytic activity of modified titanium dioxide. Nitrogen was incorporated into mesoporous TiO₂ using Sol-gel method. The N-TiO₂ was characterized using X-ray diffraction (XRD), Fourier Transform infrared spectroscopy (FTIR), Transmission electron microscopy (TEM), Scanning electron microscopy (SEM) thermogravimetric analysis (TGA), and U-Vis diffuse reflectance spectroscopy (DRS). 1%wtN-TiO₂ expresses the highest photoactivity in UV light compared to 3%wtN-TiO₂ and 5%wt N-TiO₂ respectively. The photodegradation efficiency of the catalyst follows the following trend 1%wtN-TiO₂ > 3%wtN-TiO₂ > 5%wtN-TiO₂ > PURE-TiO₂. The results obtained from the kinetics investigation shows the following trends 1%wtN-TiO₂ is 0.049 s⁻¹, 3%wtN-TiO₂ is 0.0289 s⁻¹, 5%wtN-TiO₂ is 0.0143 s⁻¹, and the PURE-TiO₂ is 0.0118 s⁻¹. The consistency in the rate constant values of the phodegradation of methylene blue; it clearly showed that the reaction follows a pseudo-first order kinetics.

Keywords: Photocatalyst, methylene blue, N-TiO₂, degradation, nanomaterials.

INTRODUCTION

The energy that the Earth receives from the Sun is about 3×10^{24} joules a year, which is nearly 10,000 times more than the global energy consumption (Chao, 2014). The photocatalytic reactions may occur homogeneously or heterogeneously, but heterogeneous photocatalysis is by far more intensively studied in recent years because of its potential use in a variety of environmental and energy-related applications as well as in organic syntheses, which include disinfection of water and air, mineralization of organic pollutants, production of renewable fuels, and organic synthesis. Heterogeneous photocatalysis using semiconductors such as titanium dioxide (TiO₂) has been one of the most widely studied. The favorable combination of electronic structure, light absorption properties, charge transport characteristics, and excited lifetimes of some semiconductors has made possible its application as photocatalyst (Serway and Jewette, 2018; Shan *et al.*, 2008).

When the energy of incident light is larger than the band gap, electron will be excited from the valence band to the conduction band and leave a positive charge, so-called a "hole", at the valence band which can obtain electrons (Parker, 1984). Most of the separated electrons and holes recombine to release energy in the heat form; only a few can reach the surface and have the capacity to drive the reaction. To enhance the photocatalysis, electron-hole pair recombination must be restricted. This can be achieved by trapping a photogenerated electron, a photogenerated hole or both of them. This process is shown in Figure 1.

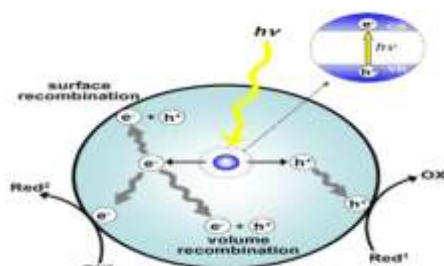


Fig 1. Photocatalytic reaction occurring on photoactivated TiO₂ particle (Mahvi *et al.*, 2009)

To overcome the above-mentioned drawback in visible light utilization, many researchers have made great efforts to modify the band structure of TiO₂ so as to shift its absorption edge towards the visible light region (Zhang, *et al.*, 2013; Yilleng *et al.*, 2018). One route for sensitizing TiO₂ to visible light so as to permit the use of the main part of the solar spectrum and also forming charge traps to keep electron-hole pairs separate is by doping pure TiO₂ with foreign ions (Nishizawa *et al.*, 2014). The doping of TiO₂ is currently attracting considerable interest as a promising route to extend the optical absorption of this material to visible spectral region. One promising approach to synthesizing visible light active photocatalyst is the substitution of titanium by transition metals, such as V, Cr, Ni, or Fe, and so on (Borgarello *et al.*, 1982; Klosek and Raftery, 2001). However, most of these metal-doped TiO₂ do not show long-term stability or do not have sufficient activities for wide range of applications. Another promising approach is the doping of non-metal atoms, such as N, S, or C (Asahi *et al.*, 2001; Zhao *et al.*, 2008). The non-metal atoms doping has been reported to be

more effective for the band gap narrowing of TiO₂ than transition metal doping (Chen *et al.*, 2007; Choi *et al.*, 1994). That is because their impurity levels are near the valence band edge of TiO₂. Therefore, they do not act as charge carriers and their roles as recombination centers are minimized compared to the metal doping (Wang and Lewis, 2005; Chen *et al.*, 2007; Choi *et al.*, 1994). Although the photoactivity of titania modified with carbon was attributed to the formation of C-doped TiO₂ depicts the formation, interstitial carbonate-doped TiO₂ and highly condensed coke-like carbon containing TiO₂ etc which acts as electron sink to reduce the rate of electron recombination (Wang and Lewis, 2005; Chen *et al.*, 2007; Choi *et al.*, 1994; Zabek and Kisch, 2010).

So many researchers begin to further investigate and use different kinds of method to prepare nitrogen-doped TiO₂ for example, Asahi *et al.* (2001) prepared N-TiO₂ material by calcination of the commercial TiO₂ at ammonia-argon atmosphere; Bang in 2005 prepared nitrogen-doped titanium dioxides using the atmospheric microwave and plasma (Hong *et al.*, 2005); Suda *et al.*, (2005) used the method of pulsed laser deposition to prepare N-TiO₂ material. Besides, it is also observed that the state of N in Titania and its effectiveness in extending the light absorption edge depend upon the way it is introduced through several preparation methods/techniques (Suda *et al.*, 2005; Viswanathan and Krishna, 2012).

Methylene blue (MB) is a cationic dye, used extensively for dyeing cotton, wool and silk. The risk of the existence of this dye in waste water may be arisen from the burns effect of eye, nausea, vomiting and diarrhea (Lang *et al.*, 2009; Hosseinnia and Keyanpour-rad, 2010). Environmental pollution on a global scale, as well as the lack of sufficient clean energy sources, have drawn much attention to the need for developing ecologically clean chemical technology, materials, and process (Coro *et al.*, 2005; Vazquez *et al.*, 2010). Cationic dyes not only impart colours to water sources but also damage living organisms by stopping the re-oxygenation capacity of water, blocking sunlight, and therefore disturbing the natural growth activity of aquatic life (Song *et al.*, 2010; Wang, 2008). The aim of this investigation was to use sol immobilization method to synthesis N-TiO₂ with enhance morphology and surface properties whose photoactivity was evaluated using methylene blue dye. and a representative evaluation of their photoactivity on methylene blue dye.

EXPERIMENTAL

Preparation of the photocatalyst (N-TiO₂)

The N-TiO₂ catalyst was prepared base on the method of described by Chakraborty and Roychudhury (2013). To prepare the N-TiO₂, 0.293g of P25 Degussa was added into 100 ml ammonia solution. To enhance homogeneous dispersion, the solution in a conical flask was placed on a magnetic stirrer at 5 revolution per minute, for 1 hour. the solution was placed in an oven and heated at 150°C for 24 h. The resulting solution obtained was then cool to 26°C. Afterward the dried solid obtained was subjected for calcination at 600°C for 2 hours. The synthesized powder of nitrogen doped titanium dioxide, was collected and labeled as 1%N-TiO₂. The same procedure was applied for preparing catalyst with 3% and 5% N-TiO₂. Using 0.898g and 1.528g respectively into the same 100cm³ volume of the ammonia. The P25 precursor sample was also treated

under the same condition using absolute ethanol as a solvent instead of ammonia and also labelled as pure-TiO₂.

Catalyst characterization

Characterization of the synthesized photocatalyst FTIR analysis was done using the SHIDMAZU FT-IR spectrophotometer. XRD analysis were carried out on a Philips X'Pert3 Analytical diffractometer, using Cu K α radiation with $\lambda=0.15406$ nm. The Crystalline structure and External morphology of the catalyst was viewed using Quanta Scanning Electron Microscope FEI Quanta 250. The measurement of transmission electron microscopy (TEM) was carried out on a FEI TecnaiTM F20 Transmission electron microscopes (TEMs) at 200kV. The optical characterization of the photocatalyst was carried out using Diffuse Reflectance UV-vis spectrophotometer equipped with a Harrick Praying Mantis TM diffuse reflection accessory used for solid samples (Perkin Elmer Lambda 6505) in the wavelength range from 250 to 800 nm with scanning speed of 300nm/min. The ultraviolet visible diffuse reflectance spectra (UV-vis DRS) of the as-synthesized samples were recorded on a UVX Radiometer (UVP Inc., Upland CA) equipped with a UVX-36 long wave sensor equipped with an integrating sphere and using BaSO₄ as the reference. The thermogravimetric analysis was performed using Mettler-Toledo TGA/DSC 1 STAR instrument with heating rate of 20°C/min in nitrogen (N₂) atmosphere.

Evaluation of the photocatalytic activity of the catalyst by degradation of the methylene blue

During the photocatalytic degradation of methylene blue (MB), 0.20g of the N-TiO₂ photocatalyst was placed into 100 ml solution of 2×10^{-5} molL⁻¹ of MB in a 250 ml conical flask, the MB solution and the catalyst was kept in the dark for 30 min before taken to the photoreactor. The absorbance of the MB was measured before irradiation and after every 20 minutes interval.

At each 20 minutes of irradiation, 10 ml of the solution would be taken out of the conical flask and centrifuged at the rate of 4000 rpm for easier isolation and removal of the used photocatalyst, then the absorbance was measured. The absorbance of the supernatant is a function of the dye concentration estimation after every 20 minutes. While the used catalyst was then characterized using FT-IR analysis after the complete 80 minutes of irradiation in the photoreactor. This is to help identified the presence of functional group corresponding to the MB fragment, which is an indicator for photodegradation activity.

RESULT AND DISCUSSION

FTIR measurement

The FTIR result of unused 1%N-TiO₂ showed Ti-O-Ti stretching observed at 401cm⁻¹, 524.66cm⁻¹, 601.81cm⁻¹, 671.25cm⁻¹, and 717.54cm⁻¹, while 879.57cm⁻¹ band corresponding to Ti-O vibrational stretching. Both as a function of the incidence angle and of the heat-treatment temperature resulting from the muffle furnace. A band was observed at 1627.97cm⁻¹ which is associated with N-H bend of the ammonia molecule. N-H asymmetric stretching vibration was observed at 3402.54cm⁻¹. At 3688.02cm⁻¹, 3757.46cm⁻¹ and 3865.48cm⁻¹ bands correspond to O-H stretch of hydrogen bonded of water molecule in the ammonia solution. While that of used 1%N-TiO₂ after the 80 minutes irradiation in addition to common peaks to

that of the un-use with C-N stretching of an aliphatic amine was observed at 1018.45cm^{-1} and another stretching was observed at 1419.66cm^{-1} due to C-C in the aromatic structure. C-H stretching of the methyl groups at 2924.18cm^{-1} . While at 3371.68cm^{-1} and 3495.13cm^{-1} belongs to N-H stretching of the ammonia solution. At band 3880.91cm^{-1} belongs to O-H stretch of hydrogen bonded of water molecule in the ammonia solution

XRD measurement

The XRD patterns of the as-prepared 1%N-TiO₂ samples were shown in Fig.3, which contained both anatase and rutile phase, with anatase peaks predominantly re-occurring with increase in intensities. Obviously, the XRD patterns revealed that doping with nitrogen has the potential of restraining the transformation from anatase to rutile and brookite. The crystallinity was sharply improved by doping with nitrogen, which was beneficial to the enhancement of photocatalytic activity (Xie *et al.*, 2010). The crystallite size was calculated using Scherrer's formula (Zang *et al.*, 2000) according to the full width at half-maximum of the diffraction pattern.

$$D = K\lambda/\beta\cos\theta$$

Where D is the average crystal size of the sample, λ the X-ray wavelength (1.54056 \AA), β the full-width at half maximum (FWHM) of the diffraction peak (radian), K is a coefficient (0.89) and θ is the diffraction angle at the peak maximum.

The as-calculated average crystal sizes of the 1%N-TiO₂ materials were 10.40 nm. The difference in crystallite size can be ascribed to the introduction of N doping. Furthermore, the N doped sample exhibited typical structure of TiO₂ crystal without any detectable peak due to Nitrogen. The reason could be due to the fact that the nitrogen species have moved into either the interstitial positions or the substitutional sites of the TiO₂ crystal structure.

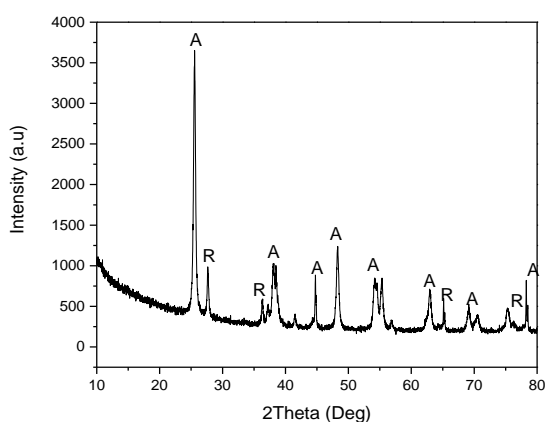


Fig. 3 XRD pattern of 1%wtN-TiO₂

SEM and TEM

The morphology of the 1%N-TiO₂ catalyst was determined using the SEM at amplification of $50\mu\text{m}$ as depicted on Fig. 4(a). The particulate size was approximated to be around 8~13 nm, with a spherical shaped as depicted on Fig 4(b) on a higher magnification of 10nm. That is because some aggregation has occurred during the synthesis process. The TEM image also depicts the nanocrystal lattice fringes of TiO₂ (101)

crystallographic planes with lattice space of 0.36nm when measured with image J software as shown in the insert of Fig 4 (b)

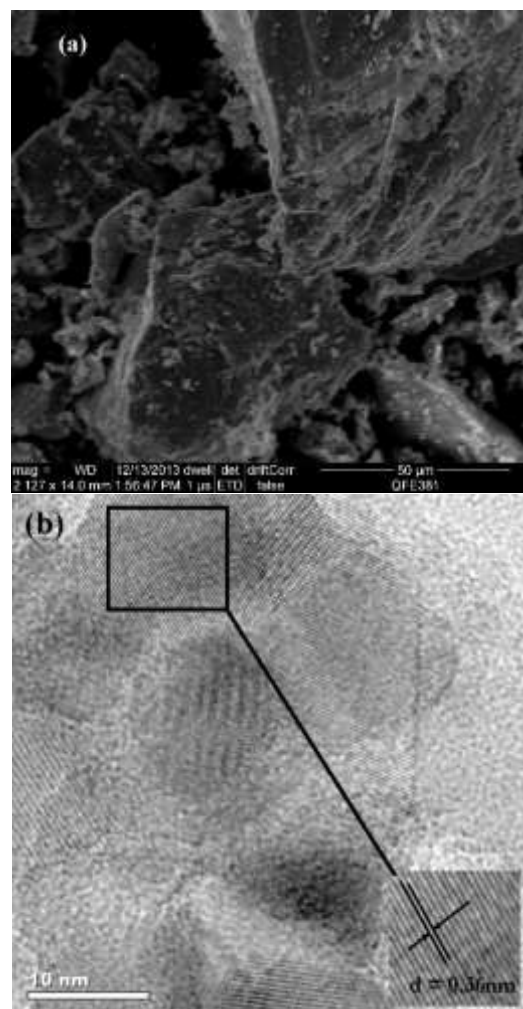


Fig. 4: (a) SEM and (b) TEM image 1N-TiO₂

TGA measurements

The TGA result showed the weight loss of the sample during calcination. Two step weight loss was observed. In the first step the main weight loss is between 60 and 86°C which corresponds to the removal of volatiles solvents like n-hexane, methanol and 1-butanol that were used in the preparation of the catalyst. The second step is a weight loss between 124 to 302°C which is due to adsorbed water, and loss accompanied with collapse of inter-agglomerate and escape of trace moiety during the phase transformation from anatase to rutile (Hermann, 2005)

Diffuse reflectance UV-Vis measurement

The UV-vis absorption spectra of the as-synthesized samples in Fig. 6. Doping Titania with N greatly enhanced the absorption of N-TiO₂ sample in the UV-vis spectrum and effectively extended the absorption edge into visible light region. Such an absorbance enhancement in the visible-light range was

consistent with the yellowish colour characteristic of the N-TiO₂ sample. The N-TiO₂ sample exhibited two kinds of characteristic light absorption edges in the DRS curves of the N-TiO₂ sample. One was in UV region attributable to the intrinsic band gap of TiO₂, while the other originated from the new energy level in the forbidden band of TiO₂ formed by N doping. The sample exhibit a shift in the optical absorption edge toward the visible region on N-TiO₂, which indicated that the nitrogen species occupied some oxygen positions in the lattice of N-TiO₂.

The band gap was calculated using plank's equation

$$\text{Band gap energy}(E) = \frac{hc}{\lambda}$$

But where c = speed of light = 3×10^8 m/s
and λ = wavelength = 451 nm

Therefore,

$$\text{Bandgap} = 2.75 \text{ eV}$$

Therefore, the optical band gap is 2.75 eV for the N-TiO₂ nanoparticles. The narrow band gap, caused by localized Nitrogen 2p states in the band structure in the form of substitutional and interstitial N states, allowed the enhancement of visible light photocatalytic activity.

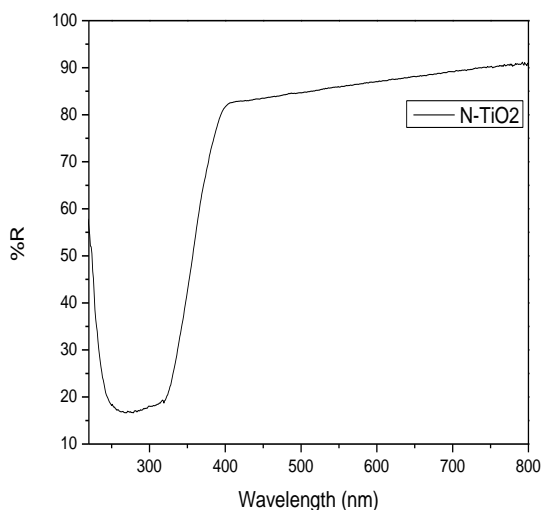


Fig. 6 Diffuse reflectance UV-Vis spectra

Photocatalytic degradation of methylene blue dye by 1%wtN-TiO₂

The first 20 minutes of irradiation of the methylene blue solution with the catalyst acts effectively with 1% wtN-TiO₂ efficiently degrading compare to 3% wtN-TiO₂, 5% wtN-TiO₂ and pure-TiO₂, but for the rest of the time i.e. from 40 minutes to 60 minutes there was a gradual reduction on the N-TiO₂ photocatalyst activity compared to the other three catalyst. Between 60-80 minutes of the Ultraviolet light irradiation all the N-TiO₂ photocatalyst were almost deactivating. From this observation it can be infer that above 80 minutes of irradiation the catalyst would deactivate completely. This drawback using ammonia as N precursors is its chemisorbed nature on TiO₂

surface, which might cover the photoactive sites that served as Lewis bases to capture photo-induced holes; this is detrimental to the oxidative degradation. That might diminish the overall photoactive promoting effect of the N doping, which shows constancy in the rate constants of the reaction for each prepared photocatalyst in the degradation of methylene blue dye for the 80 minutes of irradiation with respect to first order equation. This means that the pseudo-first order kinetic of dye removal is acceptable for this photocatalytic process. The photoactivity of the catalysts follow the trend 1%wtN-TiO₂ > 3%wtN-TiO₂ > 5%wtN-TiO₂ > Pure-TiO₂.

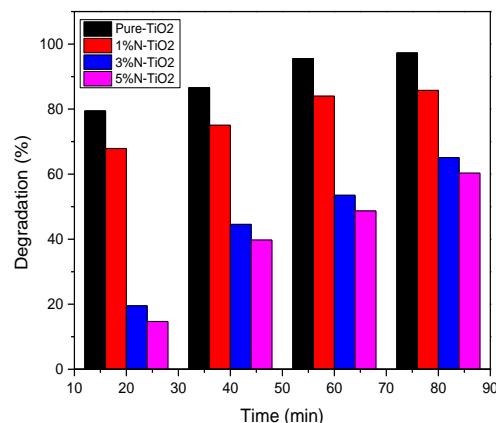


Fig. 7 Rate of photocatalytic degradation of methylene blue dye using 1% wt, 3% wt, 5% wtN-TiO₂ under UV-light irradiation

Kinetics of methylene blue dye degradation.

According to the kinetics studies shown in Fig. 8 i.e. the plot of $-\ln C/C_0$ of MB versus irradiation time for photocatalytic degradation using 1% wtN-TiO₂, 3% wtN-TiO₂, 5% wtN-TiO₂ and PURE-TiO₂ photocatalyst reactions. The mineralization of the methylene blue dye obeys a linear pattern with a good precision in all cases. Which shows constancy in the rate constants of the reaction for each prepared photocatalyst in the degradation of methylene blue dye for the 80 minutes of irradiation with respect to first order equation. This means that the pseudo-first order kinetic of dye removal kinetic is acceptable for all photocatalytic processes [28], but comparison of the lines rate constants 0.049, 0.0287, 0.0143 and 0.0118 s⁻¹ corresponding to 1%NTiO₂, 3%N-TiO₂, 5%N-TiO₂ and PURE-TiO₂ photocatalysed reaction which is the apparent rate constant show that 1%N-TiO₂ > 3%N-TiO₂ > 5%N-TiO₂ > PURE-TiO₂ catalysed reaction photoactivity follow the trend indicated in the photocatalytic degradation at the same conditions.

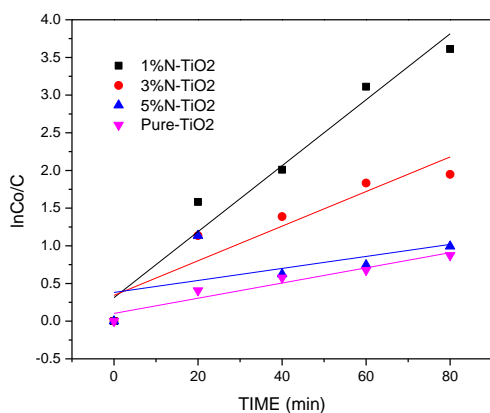


Fig. 8: Kinetics of photocatalytic degradation of methylene blue dye

CONCLUSION

Conclusively, the nitrogen content significantly affects the properties of doped TiO₂ photocatalyst. Optimally 1%wt N-TiO₂ effectively controls the particle growth and agglomeration, surface area, band gap, etc. The TiO₂ doped with 1% by weight nitrogen was the efficient photocatalyst showing best physicochemical properties (stable anatase phase with smallest crystallite and particle size, narrow particle size distribution, uniform morphology of particles and highest surface area) and efficiently photocatalytic activity in methylene blue dye.

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