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Study of Photodegration of Methylene Blue Using Nitrogen Doped Tio$_2$ Nanoparticles

Jyoti S. Bharambe*[1], Prajakta Borgaonkar[2], V.B. Pujari[3], Rajendrakumar B. Ahirrao[4]

1. ICLES' M.J. College of Arts Science and Commerce, Vashi, Navi Mumbai, MS India, jyotibharambe@yahoo.com
2. Vikas College of Arts, Science and Commerce, Vikhroli, Mumbai, MS India, prajb1@yahoo.com
3. Karma veer Bhaurao Patil College Vashi, Navi Mumbai, MS India, pujarivb @kbpcollegevashi.edu.in
4. Uttamrao Patil Arts and Science College, Dahiwel, Dhule, MS, India, ahirraorb@gmail.com

***Abstract*: Pure and N-doped TiO$_2$ nanoparticles for different dopant concentrations were synthesized by sol gel method. The samples were characterized for morphological and elemental analysis using Scanning Electron Microscope (SEM), and Energy Dispersive X-ray Spectroscopy (EDX), X-ray diffraction and Micro-raman spectroscopy and Optical properties by UV-Vis diffuse reflectance spectra. The Photocatalytic activity of the samples for methylene blue degradation was investigated under Xenon lamp and halogen lamp. 3N-doped TiO$_2$ showed narrower band gap (2.98 eV) than undoped TiO$_2$ (3.18 eV). As a result, it was observed that the photocatalytic activity of N-doped TiO$_2$ nanoparticles was higher than that of undoped TiO$_2$**

***Index Terms:* N-doped TiO$_2$, Sol-Gel method, Photocatalytic degradation, Methylene blue.**

I. INTRODUCTION

The Textile industries are the greatest polluters dumping large quantity of polluted water especially dye solutions, in the environment. These textile dyes constitute one of the largest groups of organic pollutants that are toxic to microorganism, aquatic life and human beings (Akpan U.G., 2009). How to eliminate such contaminants in water arouses a hot spot in today's scientific research. Photocatalytic degradation of effluents is the simple and environment-friendship technology and has developed rapidly in recent years. TiO$_2$, as a promising semiconductor photocatalyst, has been widely used in wastewater treatment on account of its unique photo-electric properties, high chemical stability, cost benefit and safety toward both humans and the environment. However widespread applications of TiO$_2$ as photocatalysis have been limited due to its wide band gap (~ 3.2 eV) (Modanlu S. & Shafiekhani A., ;2019). It requires U.V radiation of Wavelength less than 387 nm for photocatalytic activity. With TiO$_2$ only 3-5% of solar radiation reaching the earth's surface can be used (Zhang, Min;2013). Thus, for efficient photocatalytic activity it is necessary to extend the photoresponse of TiO$_2$ in the visible region by modification of its optical properties. Another problem is the high recombination rate of the photogenerated electron hole pairs which can be limited by introducing charge traps for electron and or holes which prolongs the recombination rate (Sharotri, N., et al.,2019).

In order to optimize the photocatalytic performance of TiO$_2$, different preparation methods (Andrew M., et al.,1997) and a lot of modification methods have been tried but doping TiO$_2$ with foreign ions is one of the most promising strategies for sensitizing TiO$_2$ to visible light and also for forming charge traps to keep electron hole pairs separate (Fujishima A, et al.,2008). TiO$_2$ doped with transition metals like Cr, Fe, V, Mn, Cu, Zn, Ni (Yoong. L., et al., 2009) have been used in past to improve visible light absorption. However, these metals have to be doped in small quantity to avoid recombination of photogenerated electron and hole favored by these dopant species (Asahi, R., et al.,2001) But the low content of metal doping leads to only small shift of absorption edge towards visible region. Generally, metal dopants form energy level below the conduction band edge (Kang, X.et al.,2019). Nitrogen doping is quite encouraging because of its its similar size (155 pm) to oxygen (152 pm), small ionization energy and stability. 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 enhance photocatalytic activity compared to bare TiO$_2$ (Pawar, S.G., et al.,2011; Mingjie S., et al.,2020).

In this work, pure TiO$_2$ and N-doped TiO$_2$ nanoparticles were synthesized by sol gel method and the influence of N content on the photocatalytic performance tested by the photocatalytic degradation of methylene blue was discussed.

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II. EXPERIMENTAL

Pure TiO_2 and a series of N-doped TiO_2 with different nitrogen amount were prepared by sol–gel method using titanium butoxide [Ti $(OC_4H_9)_4$] as the precursor and nitric acid (HNO_3) as the catalyst. The molar ratio of Ti $(OC_4H_9)4/H_2O$/ethanol/HNO_3 was kept at about 1/30/20/0.1. The preparation of pure TiO_2 photocatalyst was carried out by sol-gel method using titanium butoxide [Ti $(OC_4H_9)_4$] as the precursor and Nitric acid (HNO_3) as the catalyst. During the process, 8.6 ml of Titanium butoxide was mixed with 20 ml of ethanol (C_2H_5OH) and vigorously stirred for 1 hour at room temperature to obtain solution A. Further 4.5 ml of deionised water, 20 ml of ethanol and x ml (x=0.1, 0.2, 0.3) of nitric acid were mixed together to generate solution B. Then the solution B was added dropwise into the solution A under the magnetic stirring for 1 hour and the resultant solution was stirred for further 1 hour at room temperature to increase homogeneity. The solution was kept for 48 hours at room temperature for gelation and dried by heating at 100^{o}C for 3 hours to remove the excess solvent. After grinding by mortar pestle, the resultant powders were calcined at 500 ^{o}C for 2 hours.

N-doped TiO_2 for different molar ratio of nitrogen source to titanium precursor (N/Ti=0.5, 1, 2 and 3%) were synthesized by adding dopant precursor Triethylamine in solution A.

III. CHARACTERIZATION

The morphology, phase and crystallinity identifications of the samples were performed with SEM (using VEGA MV 2300/T40), powder XRD (using Philips X´ Pert X-ray diffractometer with Cu Kα radiation of wavelength 1.54056 Å under the operating conditions of 40 kV and 30 mA) and micro-Raman spectroscopy (Renishaw equipped with a 514 nm laser) respectively. The band gap of TiO_2 was determined by measuring UV-VIS diffuse reflectance spectra on Cary 500 UV –NIR spectrophotometer in the range of 200 nm to 800 nm.

The photocatalytic activity of the samples was investigated by degrading an organic pollutant in form of Methylene Blue (MB) dye. This dye is one of the common dyes extensively used in various industrial applications. For photodegradation of methylene blue dye 15 mg of photocatalyst was added to aqueous solution of methlylene blue (1.6 mg/lit) in the quartz beaker. The solution was allowed to stir for 15 minutes to obtain adsorption equilibrium. The photoactivity experiments were performed by using two light sources. In the first 50 W Xenon lamp is used as a UV-vis emitting light source, while 150 W of halogen lamp was used as an visible light source. Both lamps were used without cut-off filters. The distance between the beaker and the light source was kept about 10 cm. The photocatalytic activity was determined by measuring the normalised intensity of the absorption band at 665 nm using NIR spectrophotometer and plotted as a function of irradiation time.

IV. RESULTS AND DISCUSSION

A) *Scanning Electron Microscopy (SEM) and Energy Dispersive Spectrometry (EDS)*

Microstructure of N-doped TiO_2 photocatalyst and their surface morphologies for different concentrations were studied by SEM equipped with EDS. SEM images 1N-doped TiO_2 is presented in Figure 1. SEM images shows uneven distribution of agglomerated particles with spherical shape. EDS mapping indicated that N, element was highly and uniformly dispersed on the photocatalyst surface. As the molar ratio of dopant to Ti increases the higher concentration of dopant was observed on the surface. Thus, EDS analysis confirms that N have been incorporated into synthesized samples and their EDS values are given in Table 1.

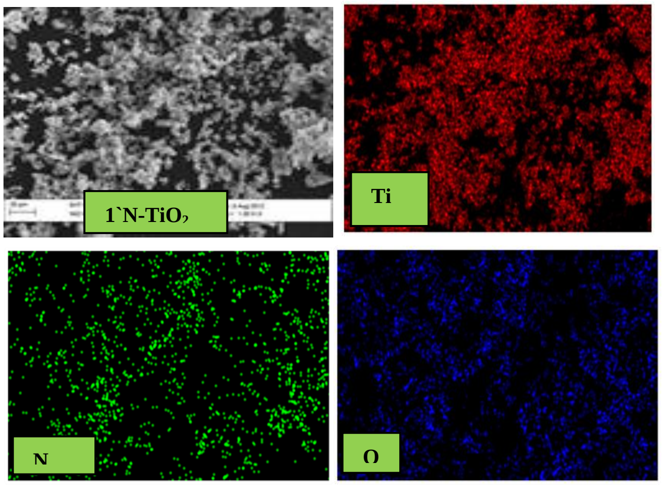


Fig.1. SEM micrograph and elemental mapping of 1N-TiO_2

Table 1. EDS values of different doping concentrations of N in TiO_2

Sample	1N-TiO_2		2N-TiO_2		3N-TiO_2	
	(wt%)	(at%)	(wt%)	(at%)	(wt%)	(at%)
Ti	65.13	37.87	44.61	19.60	63.10	36.12
O	32.22	50.1	37.63	49.49	34.06	58.34
N	0.23	0.45	0.67	0.97	2.83	5.3
C	2.43	5.63	17.01	30.01		

B) *X-Ray diffraction*

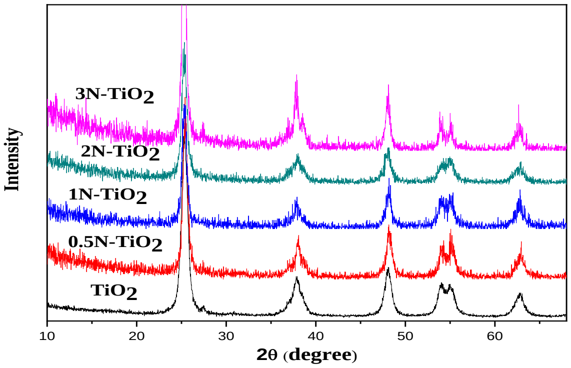


Fig.2. X-ray diffraction pattern of N-doped TiO2 with different N/Ti ratios

The functionality of TiO_2 photocatalyst for various applications depends on the crystal phase. It is therefore important to understand the modification in the crystal structure by incorporation of the dopants in TiO_2.

The XRD diffraction patterns of N-doped TiO_2 nanoparticles synthesized with various concentrations of N are shown in Fig 2. The pure TiO_2 was composed of primarily anatase phase under the processing conditions. 25.38, 48.1, 54.1, 55.2, 62.7, 68.9, 70.2, 75.29, 83 attributed to the planes (101), (004), (200), (105), (211), (118), (116), (220) of anatase phase of TiO_2. The crystallites are randomly oriented and the d values calculated for the diffraction peaks are in good agreement with those given in JCPD data card. (JCPD no. 78-2485.

The anatase phase has been retained without phase change after N doping. The diffraction peaks are much sharper with stronger intensity that indicates the increase of average crystallite size. The crystallite sizes of TiO_2 for different N/Ti ratios are given in Table 2. No new diffraction peaks are observed in the N-containing phase. In addition, there is no change in d-space values which indicates that N has been introduced into the lattice without changing the average unit cell dimension. The crystallite size of N-doped samples varies between 12 nm and 16 nm.

Table 2 Crystallite size, anatase and rutile fraction and energy band gap of undoped TiO2, N-doped TiO2

Sample	Crystallite size (nm)	Lattice constant		Band Gap eV
		a(nm)	c(nm)	
TiO_2	9.62	3.778	9.478	3.08
0.5N-TiO_2	12.93	3.766	9.448	3.03
1N-TiO_2	13.13	3.781	9.480	3
2N-TiO_2	11.47	3.783	9.476	2.94
3N-TiO_2	16.28	3.789	9.508	2.88

C) Raman Spectra

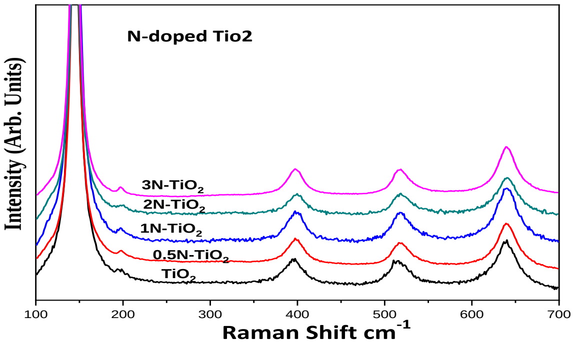
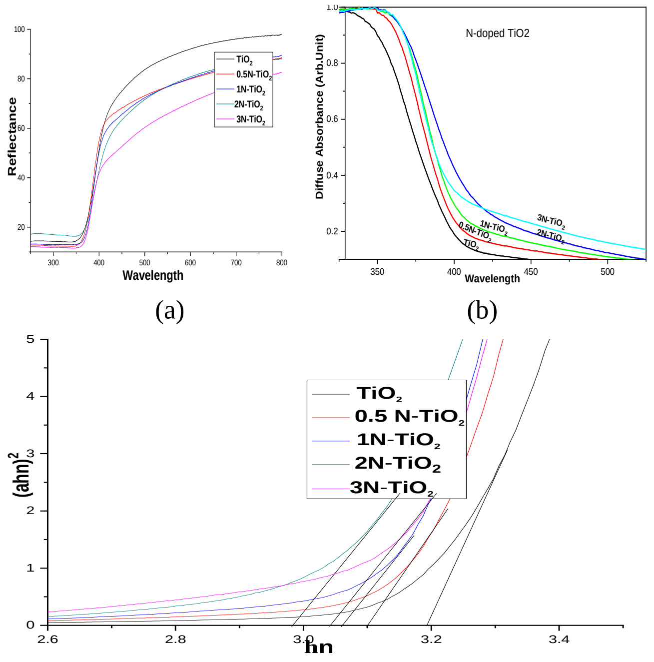


Fig.3. Raman spectra of N-doped TiO_2 with different N/Ti concentrations

Raman spectroscopy is a powerful technique for the investigation of phase on the surface of TiO2 Raman spectra of pure TiO2 and N-doped TiO2 are shown in Fig. 3. Raman spectra of N-doped TiO_2 samples with different molar ratios indicate peaks at 145, 197, 399, 520 and 640 cm^{-1} corresponding to $E_{g(1)}$, $E_{g(2)}$, $B_{1g(1)}$, $B_{1g(2)}$ and $E_{g(3)}$ vibration energies, respectively, of anatase phase. This signifies that surface of N-doped TiO_2 is predominantly composed of anatase phase structure.

D) UV-vis Diffuse Reflectance Spectroscopy

The UV-vis diffuse reflectance and absorption spectra of undoped TiO_2 and N-doped TiO_2 nano materials with different doping concentrations are shown in Fig 4(a) & (b). The band gap energy of each sample was determined from the tangents line in the plots of Kubelka Munk function $(\alpha h\nu)^2$ verses energy of the exciting light hν as shown in Fig 4(c) and are summarized in Table 2. With increasing dopant concentration an increased absorbance in the visible spectrum was observed.



(a) (b)

(c)

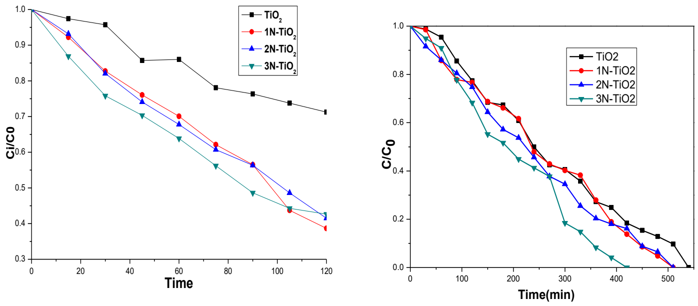
Fig. 4. (a, b &c) Diffuse reflectance spectra of N-doped TiO_2 with different doping concentrations. (a)Reflectance (b) absorbance (c) $(\alpha h\boldsymbol{\nu})^2$ vs h$\boldsymbol{\nu}$

The absorption edge of the samples showed slight shift towards higher wavelengths for TiO_2, mainly responsible to midgap (N-2p) level above the (O-2p) valance band formed by oxygen lattice sites substituted by nitrogen atoms. At higher N/Ti molar ratio the density of states of these N 2p states increases to overlap with O-2p states and causes upwards shift of valance band. In addition, the introduced oxygen vacancies cause charge imbalance between O^{2-} and N^{3-} ions that are also responsible for visible light absorption in N-doped TiO_2 [10,]. The greatest shift was observed with the sample 3N-TiO_2.

E) Photocatalytic Activity

The photocatalytic activities of N-doped TiO_2 samples were evaluated through the photodegradation of Methylene blue under 50 W Xenon lamp and 150 W Halogen lamp and was compared with pure TiO_2 powder.

The photocatalytic activity of N-doped TiO_2 enhances with concentration of nitrogen and is maximum for 3% N/Ti molar ratio as shown in Fig. 5(a).(b) and Fig(6). Enhanced photocatalytic activity of N-doped TiO_2 could be due to narrowed band gap derived from the mixing of N-2p and O-2p states. N-doped showed less activity in halogen lamp than in xenon lamp.



(a) (b)

Fig. 5. Photodegradation of Methylene blue for N-doped TiO_2 samples in (a) Xenon lamp and (b) Halogen lamp

The Photodegration rate of TiO_2, N-doped TiO_2 in xenon lamp and halogen lamp is given in Table. 3.

From the above results it seems that 3N-TiO_2 showed highest photocatalytic activity.

Table 3. Photodegration rate of TiO_2, and N-doped TiO_2 in xenon lamp and halogen lamp

Sample	Xenon	Halogen
TiO_2	0.002668	0.002854
1N-TiO_2	0.006537	0.003193
2N-TiO_2	0.006454	0.003628
3N-TiO_2	0.008038	0.004208

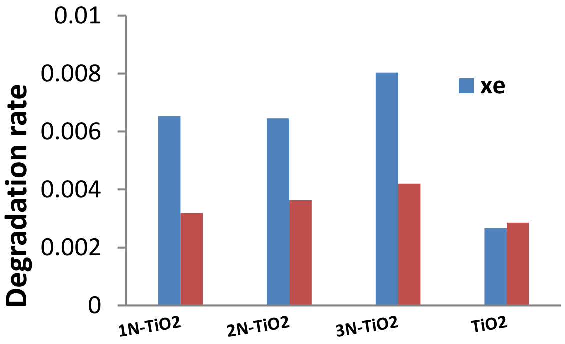


Fig 6. The Photodegration rate of methylene blue catalyzed by N-doped TiO_2 photocatalyst

CONCLUSION

N-doped TiO_2 photocatalyst with different doping concentrations were prepared by sol gel method. The effect of doping concentrations on structural, morphological, optical properties were studied by SEM-EDS analysis, Raman spectroscopy, XRD, and DRS. The XRD revealed that all the samples had good crystallisation with maximum anatase phase structures and with the particle size of about 12 nm to 16 nm. The absorption edge of the samples shifts towards higher wavelengths with increasing dopant concentration to decrease the energy band gap to 2.98 eV for N-doped TiO_2. The photocatalytic activity of the N-doped TiO_2 samples was investigated by degrading an organic pollutant Methylene blue under Xenon lamp and Halogen lamp by measuring the normalised intensity of the absorption band at 665 nm which showed that 3N-TiO_2 has higher photodegradation rate in both xenon and halogen lamp.

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