

## VISIBLE-LIGHT-ACTIVE NITROGEN DOPED $\text{TiO}_2$ NANOPARTICLES PREPARED BY SOL-GEL ACID CATALYZED REACTION

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**Abstract:** Yellow-colored nitrogen doped  $\text{TiO}_2$  photocatalyst and a pure  $\text{TiO}_2$  powder were synthesized via sol-gel method using  $\text{TiCl}_4$  and urea as raw materials. However, the synthesis procedure for nitrogen doped  $\text{TiO}_2$  was catalyzed by acid that dialed with controlled precipitation and slow nucleation. According to XRD analysis, the nitrogen doped  $\text{TiO}_2$  consisted of anatase phase of titania which was a significant achievement regarding its possible photocatalytic applications. The band gaps of nitrogen doped  $\text{TiO}_2$  and pure  $\text{TiO}_2$  were estimated from UV-Vis spectroscopy data to be 2.8 and 3.3 eV, respectively. Photocatalytic properties of the nitrogen doped  $\text{TiO}_2$  nanocatalyst and pure  $\text{TiO}_2$  were compared for degradation of crystal violet dye in visible light irradiation. In comparison to pure  $\text{TiO}_2$ , nitrogen doped  $\text{TiO}_2$  showed superior photocatalytic efficiency towards the dye.

**Keywords:**  $\text{TiO}_2$ , sol-gel, band gap, nitrogen, nanoparticles.

### 1. INTRODUCTION

Titanium dioxide ( $\text{TiO}_2$ ), as a chemically stable, nontoxic, highly efficient, and relatively inexpensive photocatalyst, has been widely used for water and air purification since many environmental pollutants can be degraded by oxidation and reduction processes on  $\text{TiO}_2$  surface [1- 3]. However, the  $\text{TiO}_2$  photocatalyst has not been applied widely in the field of environmental pollution control, since its large band gap energy ( $E_g = 3.2$  eV) considerably limits the utilization of natural solar light or artificial visible light. Modification of  $\text{TiO}_2$  to extend its absorption edge toward the visible light region has been the subject of recent research [4].

$\text{TiO}_2$  was used as visible light photocatalysts by substitution doping of metal ions, ion implantation, organic dye sensitization, and hydroxide or surface coordination. However, these modified photocatalysts, in general, show a weak absorption in the visible light region and deactivate easily.

Band-gap narrowing by the introduction of nonmetal anions (N, C, S and F) into  $\text{TiO}_2$  was recently found to be more efficient than the traditional methods to yield catalyst with high catalytic activity under visible light irradiation [5]. Theoretical calculations showed that the p-orbitals of these dopants significantly overlapped

with the valence band O 2p orbitals, which facilitated the transport of photo-generated charge carriers to the surface of the catalyst [1].

In earlier reported studies, N doping of  $\text{TiO}_2$  is achieved by different methods such as treating anatase  $\text{TiO}_2$  powders in an  $\text{NH}_3/\text{Ar}$  atmosphere [6], solution based methods like precipitation [7,8], sol-gel [9,10], solvothermal [11], hydrothermal processes [12] and direct oxidation of the dopant containing titanium precursors at appropriate temperatures [13].

In this work nitrogen doped  $\text{TiO}_2$  photocatalyst prepared via slow nucleation sol-gel method and crystal violet (CV, a kind of triarylmethane dye, Scheme 1.) chose as the target compound at photocatalytic studies.



Scheme 1

## 2. EXPERIMENTAL

### 2. 1. Materials and Reagents

The chemicals used in this study were titanium tetrachloride ( $\text{TiCl}_4$ , 99.9%), Fluka, as a titanium precursor, urea ( $\text{H}_2\text{NCONH}_2$ , 98%), silver nitrate ( $\text{AgNO}_3$ ), crystal violet ( $\text{C}_{25}\text{H}_{30}\text{N}_3\text{Cl}$ ), hydrochloric acid and anhydrous ethanol ( $\text{C}_2\text{H}_5\text{OH}$ ) from Merck. All reactant were used without further purification.

### 2. 2. Nitrogen Doped $\text{TiO}_2$ and Pure $\text{TiO}_2$ Preparation

Nitrogen doped  $\text{TiO}_2$  and pure  $\text{TiO}_2$  were prepared by the sol-gel method. For nitrogen doped  $\text{TiO}_2$  preparation, 2 mL  $\text{TiCl}_4$  was added to a 0.5 N hydrochloric acid solution under vigorous stirring in an ice water bath. Then 30 grams urea was added to reaction vessel. The mixture was stirred at 105 °C for 7 hours. After cooling at room temperature, the resulting solid was collected by filtration and washed with distilled water for several times. After washing, no  $\text{Cl}^-$  ion was detected by the reaction with 0.1 N  $\text{AgNO}_3$  solution. The produced powder dried at 100 °C then calcined for 5 h at 450 °C.

The pure  $\text{TiO}_2$  was prepared with the same method except no using hydrochloric acid and denoted as T photocatalyst.

### 2. 3. Characterization of the Products

Spectroscopic analyses of Nitrogen doped  $\text{TiO}_2$  and pure  $\text{TiO}_2$  samples were performed using UV-vis spectrophotometer (Shimadzu UV 2100) and Bruker, Eqinox 55 FT-IR spectrometer. Crystallite size, and phase identification of the product were characterized by X-ray diffraction (XRD) obtained on Philips X-pert diffractometer using a scan rate of 21/min and Cu Ka line ( $\lambda=1.54056 \text{ \AA}$ ) radiation with working voltage and current of 40 kV and 40 mA, respectively. The morphology of the product was studied by scanning electron microscopy (SEM, Philips XL30). The (BET) specific surface area of the sample was determined through nitrogen adsorption (Micromeritics, Gemini 2370). TG-DSC was carried out using STA 150 Rhenometric Scientific unit. Measurements were

taken with a heating rate of 10 °C/min from 25 to 800°C in argon atmosphere.

### 2. 4. Photocatalytic Activity Determination

When photocatalyst nanoparticles adsorb light, it will generate electron-hole ( $e^-h^+$ ) pairs which are able to initiate oxidation and reduction reactions to destroy the organic molecules. Photocatalytic activities of the prepared nitrogen doped  $\text{TiO}_2$  and pure  $\text{TiO}_2$  photocatalysts were evaluated by the degradation of crystal violet dye (CV) under visible light. For all photocatalytic experiments, a cylindrical glass was used as the reactor, which was filled with 300mL of aqueous suspension of CV (5 ppm) containing 1 g/L of photocatalysts. It was an open Pyrex glass tube with double walls, so that a jacket of water was cooling the reactor to constant temperature at  $25 \pm 1$  °C. An Osram lamp was used as the light source. Figure 1 shows the emission spectrum of Osram lamp. It was placed in a quartz vessel and immersed in center of photo reactor. Air was continuously bubbled into the solutions by an aquarium pump in order to provide a constant source of dissolved oxygen. Prior to irradiation, the suspension was magnetically stirred in the dark for approximately 30 min to ensure establishment of an adsorption/desorption equilibrium among the photocatalyst particles, CV, and atmospheric oxygen. During the course of visible light irradiation, a suspension of about 5mL was taken out after regular intervals, centrifuged, and then filtered through a Millipore

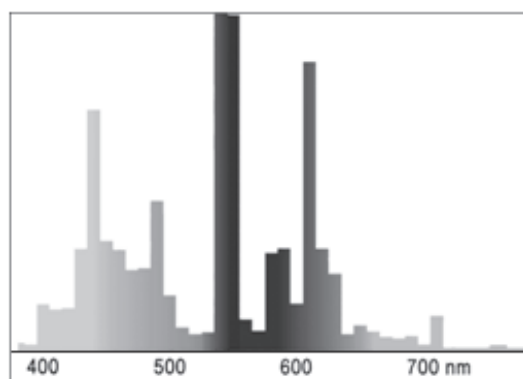


Fig. 1. Emission spectrum of Osram lamp.

filter. The filtrates were then studied by UV–vis spectroscopy.

### 3. RESULTS AND DISCUSSION

#### 3. 1. Photocatalysts Characterization

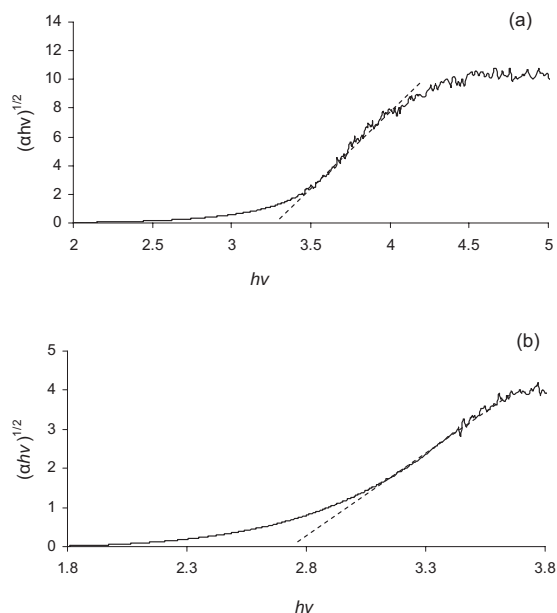
The optical band gap ( $E_g$ ) in a semiconductor was determined by plotting  $(\alpha h\nu)^{1/m}$  versus photon energy ( $h\nu$ ) where  $\alpha$  represents optical absorption coefficient and  $m$  represents the nature of transition. Now,  $m$  may have different values, such as  $1/2$ ,  $2$ ,  $3/2$  or  $3$  for allowed direct and indirect transitions, respectively [14, 15]. The plots of  $(\alpha h\nu)^{1/2}$  for allowed indirect transitions of prepared pure  $\text{TiO}_2$  (a) and nitrogen doped  $\text{TiO}_2$  (b) samples dispersed in ethanol versus photon energy are shown in Figure 2 a and b. According to Figure 2 a, the extrapolated optical absorption gap of the pure  $\text{TiO}_2$  is found to be 3.3 eV at room temperature. This is in agreement with the literature values for anatase  $\text{TiO}_2$  [16, 17]. Similarly, as shown in Figure 2 b the optical absorption gap of nitrogen doped  $\text{TiO}_2$  was found to be 2.8 eV. The visible light absorbance of nitrogen doped  $\text{TiO}_2$  is of great significance for its practical application point of view.

The estimated indirect band gap of the prepared nitrogen doped  $\text{TiO}_2$  reveals 0.5 eV red shift from value obtained for prepared pure  $\text{TiO}_2$ . The smaller band gap of the nitrogen doped  $\text{TiO}_2$  in comparison to band gap value of pure  $\text{TiO}_2$  is presumably due to the substitution of the lattice oxygen by nitrogen and formation of oxynitride center [18].

Figure. 3 shows the FTIR spectra of prepared nitrogen doped  $\text{TiO}_2$  and pure  $\text{TiO}_2$  samples. The broad peaks in the range  $3000\text{--}3400\text{ cm}^{-1}$  and  $1630\text{ cm}^{-1}$  originated from surface adsorbed water and surface hydroxyl groups [19,20]. The peak in between  $1250\text{ to }1500\text{ cm}^{-1}$  could be attributed to the entered nitrogen species in  $\text{TiO}_2$  network [21, 22].

The crystalline structures of synthesized samples were investigated by XRD measurements. The XRD patterns obtained for nitrogen doped  $\text{TiO}_2$  and pure  $\text{TiO}_2$  samples are shown in Figure 4, curve a and b, respectively.

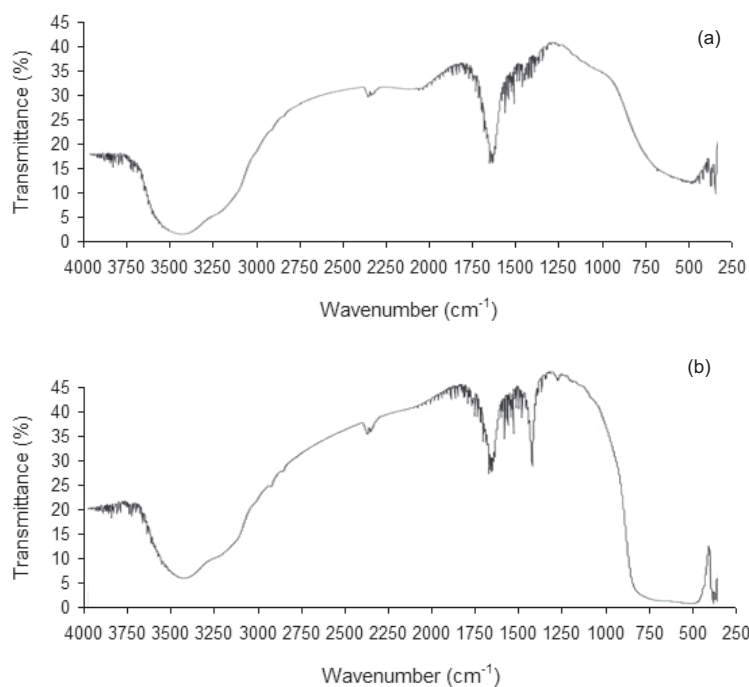
The XRD patterns of the nitrogen doped sample can be assigned to pure anatase  $\text{TiO}_2$  with



**Fig. 2.**  $(\alpha h\nu)^{1/2}$  as a function of photon energy for prepared pure  $\text{TiO}_2$  (a) and nitrogen doped  $\text{TiO}_2$  (b) samples dispersed in ethanol.

reflection peaks in  $(1\ 0\ 1)$ ,  $(0\ 0\ 4)$ ,  $(2\ 0\ 0)$ ,  $(1\ 0\ 5)$  and  $(2\ 1\ 1)$  crystal planes. However, the diffraction peaks for the pure  $\text{TiO}_2$  sample can be ascribed to a mixed phase of rutile and anatase after calcination. The transition from anatase to rutile during the preparation of nitrogen doped  $\text{TiO}_2$  was restrained by the doping of N in the lattice. This result is in agreement with the works reported by Yu and co-workers [23].

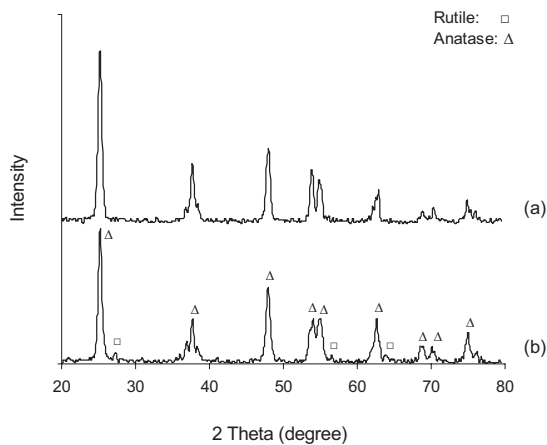
The average crystallite size of the synthesized nitrogen doped  $\text{TiO}_2$  and pure  $\text{TiO}_2$ , calculated from the XRD data, according to Scherrer's equation,  $D = 0.9 \lambda / (\beta \cos\theta)$  where  $D$  is the average crystallite size (nm),  $\lambda$  is the applied X-ray wavelength ( $\lambda = 1.5406\text{ \AA}$ ),  $\theta$  is the diffraction angle and  $\beta$  is a full-width at half the maximum of diffraction line observed in radians. According to Scherrer's equation, the average crystallite sizes of pure  $\text{TiO}_2$  and nitrogen doped  $\text{TiO}_2$  samples are 17.43 and 24.07 nm,



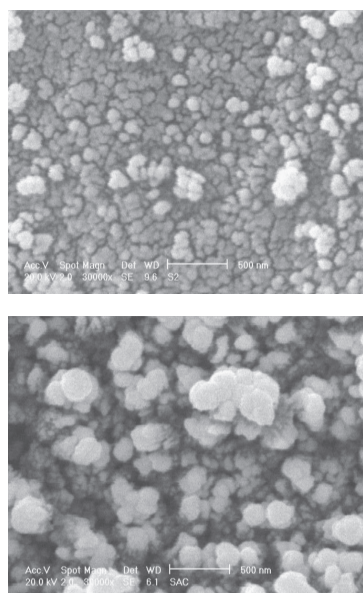
**Fig. 3.** FTIR spectra of prepared pure  $\text{TiO}_2$  (a) and nitrogen doped  $\text{TiO}_2$  (b) samples.

respectively. According to the quantum size effect theory, the band-gap of the semiconductor is very sensitive to the nanoparticle size, the smaller the semiconductor particle size, the wider the band-gap.

Figure 5 shows SEM images of prepared pure  $\text{TiO}_2$  and nitrogen doped  $\text{TiO}_2$  nanoparticles. These images confirm that both of samples



**Fig. 4.** XRD patterns of prepared nitrogen doped  $\text{TiO}_2$  (a) and pure  $\text{TiO}_2$  (b).



**Fig. 5.** SEM images of prepared pure  $\text{TiO}_2$  (a) and nitrogen doped  $\text{TiO}_2$  (b) nanoparticles.

exhibit the form of spherical particle and are to some extent agglomerated.

Figure 6 shows the  $N_2$ -adsorption isotherms as a function of  $P/P_0$ . The (BET) specific surface areas of the samples were determined through their nitrogen adsorption isotherms. According to Figure 6, both of isotherms are of type IV which proves the presence of mesopores within the synthesized samples [24, 25]. The BET surface areas of pure  $TiO_2$  and nitrogen doped  $TiO_2$  nanoparticles are 43.79 and 54.55  $m^2g^{-1}$ , respectively deduced from the plots.

Differential scanning calorimetry and thermogravimetric curves of pure  $TiO_2$  and nitrogen doped  $TiO_2$  samples are shown in Figure 7.

For pure  $TiO_2$  sample, the decrease in weight, up to 296 °C is attributed to desorption of the physisorbed water and organic residues (confirmed by three endothermic peaks on the DSC curve at about 110, 236 and 296 °C). According to TG analysis, a large number weight loss, 44.28%, is observed up to 296 °C as a result of remove of physisorbed water and organic residues. After that, the weak thermal effect at 350-500 °C is accompanied by obvious exothermic peak at around 460 °C in DSC curve which confirms the crystallization of the amorphous phase to anatase. Above 460 °C, the change in weight is very small.

For nitrogen doped  $TiO_2$  sample, removal of

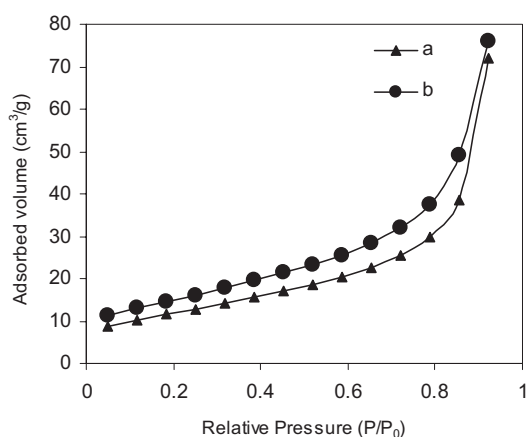


Fig. 6.  $N_2$ -adsorption isotherms of prepared pure  $TiO_2$  (a) and nitrogen doped  $TiO_2$  (b) samples.

physisorbed water and organic residues take place up to 220 °C which is accompanied by two significant endothermic peaks in DSC curve. TG analysis shows that the weight loss at 220 °C is 19.03%. The weight loss as a result of physisorbed water and organic residues at nitrogen doped  $TiO_2$  sample is smaller than pure  $TiO_2$  sample. Furthermore, a diffuse exotherm at around 350 °C in DSC curve which confirms the crystallization of the amorphous phase to anatase is not accompanied with large weight loss in the temperature range of 300-500 °C. It can be described as remaining of some nitrogen species in the nitrogen doped  $TiO_2$  network during heat treatment.

### 3. 2. Formation Mechanism of Nitrogen Doped $TiO_2$

The reaction was started by producing  $TiO(OH)_2$  as a result of slow hydrolyze of  $TiCl_4$  in an acidic solution. After that, PH slowly increased by gradually decomposition of added urea. The finding is consistent with Kuroda et al.

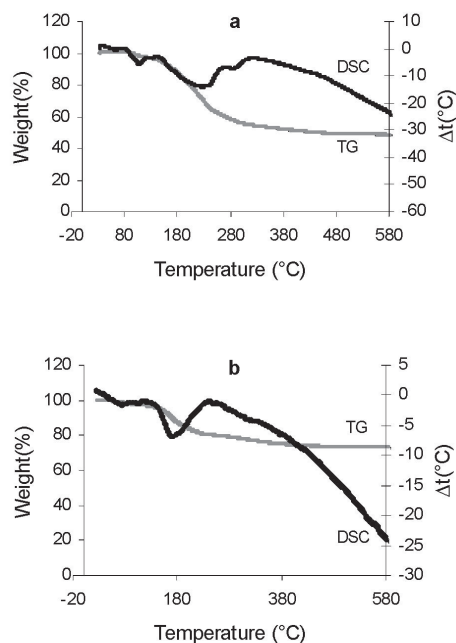


Fig. 7. TG-DSC curves of prepared pure  $TiO_2$  (a) and nitrogen doped  $TiO_2$  (b) samples.



approach which showed that  $\text{NH}_2\text{CONH}_2$  decomposed by heat treatment into  $\text{OH}^- + \text{NH}_4^+ + \text{CO}_2$  [26]. The prepared  $\text{TiO}(\text{OH})_2$  acts as a strong Lewis acid site and then adsorb the ammonia, water and other intermediate product of hydrolysis of urea [26]. Then the adsorbed species are transformed in to  $\text{NH}_2$  and  $\text{OH}$  after heat treatment and finally nitrogen is incorporated in to  $\text{TiO}_2$  lattice by dehydration and condensation reaction to form anatase  $\text{TiO}_2\text{-xNx}$ .

### 3. 3. Photocatalytic Activity

Figure 8 shows the efficiency of photodegradation (X) of the nitrogen doped  $\text{TiO}_2$  in comparison to pure  $\text{TiO}_2$  photocatalyst for the removal of crystal violet as a function of time at  $\lambda = 587 \text{ nm}$ . Here  $X = (C_0 - C)/C_0$ , where  $C_0$  is the initial concentration of dye, and C is the concentration of dye at time T. As shown in Figure 8, nitrogen doped  $\text{TiO}_2$  has high efficiency of 78% in crystal violet decolorization in 120 minutes but pure  $\text{TiO}_2$  shows no significant photocatalytic efficiency under visible light.

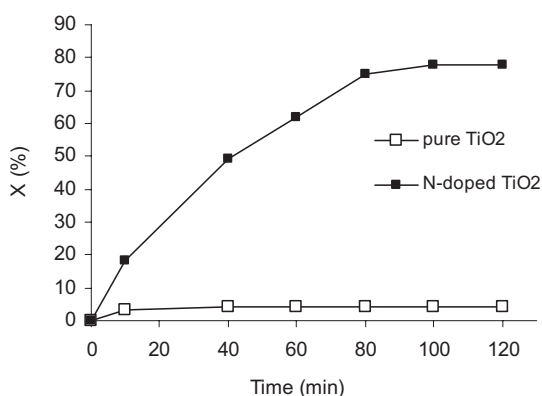


Fig. 8. The degree of photocatalytic degradation (X) as a function of irradiation time at 587 nm for pure  $\text{TiO}_2$  ( $\square$ ) and Nitrogen doped  $\text{TiO}_2$  ( $\blacksquare$ ).

### 4. CONCLUSION

Yellow-colored nitrogen doped  $\text{TiO}_2$  powder was synthesized by a simple sol-gel acid catalyst

reaction. Here the synthesis procedure deals with controlled precipitation and slow nucleation and growth of nitrogen doped  $\text{TiO}_2$  nanoparticles. The preparation of nitrogen doped  $\text{TiO}_2$  resulting in a desired band gap narrowing and an enhancement in the photocatalytic activity under visible light.

### 5. ACKNOWLEDGMENTS

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