

## TiO<sub>2</sub> Thin Film: Preparation, Characterization, and its Photocatalytic Degradation of Basic Yellow 28 Dye

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### Abstract

In this research, the thin films of N-S doped titanium dioxide (TiO<sub>2</sub>) were successfully prepared by simple sol-gel method in the presence of tetrabutylorthotitanate as a starting reagent. Furthermore, titanium dioxide (TiO<sub>2</sub>) was functionalized with thiourea. Furthermore, N-S doped titanium dioxides (NSTO) were fixed on glass balls by glass balls fixed-bed reactor system. Besides, the effect of some parameters such as volume and exit flow rate of basic yellow 28 solution on the degradation of basic yellow 28 solution under visible light irradiation were investigated. Moreover, the degradation rates were found to be strongly influenced by all the above parameters. The as-synthesized N-S doped titanium dioxides (NSTO) were characterized by X-ray diffraction (XRD), scanning Electron Microscopy (SEM), spectra energy dispersive analysis of X-ray (EDX), and ultraviolet-visible (UV-Vis) techniques. Sol-gel synthesis of titanium dioxide was favorable, because the synthesis time of sol-gel method was shorter than that of other method.

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## 1. Introduction

In recent years, the preparation of nanocrystalline semiconductor particles has been intensively pursued because thanks to increase activity and a large surface-to-volume ratio and special optical and electrical properties as compared to those of the bulk materials [1-5]. Heterogeneous photocatalysis has

received a great attention as an advanced oxidation process for the treatment of air and water streams. Industrial wastewater included the dyes are one of the important sources of environmental pollution that founded in textile industrial wastewater which are harmful for human health and environment [6-7]. Among the various semiconductor materials, TiO<sub>2</sub> nanoparticles are important photocatalyst materials

for the degradation of organic contaminants in water and air because of its high efficiency, inexpensiveness, easy production, photochemical and biological stability, and innocuity to the environment and human beings [8]. TiO<sub>2</sub> nanoparticles as photocatalysis have advantages such as strong resistance to chemicals, resistance to photo corrosion, ambient operational temperature and have led the relevant applications to the stage of commercialization. The photocatalytic activity of titania varies depending on its crystallinity, particle size, crystal phase, surface area, and the method of preparation. Different preparation methods such as hydrothermal [9] sol-gel [10], and microwave [11] to synthesize nanoparticles of titania have been reported. In presence study, N-S doped titanium dioxides (NSTO) were successfully synthesized through a two-step sol-gel method. Furthermore, photo-catalytic degradation of basic yellow 28 as azo dye was investigated through the glass balls fixed-bed reactor system in different reaction conduction such as volume of dye solution and exit flow rate of dye solution. The produced were characterized by SEM, XRD, UV-vis, and EDX.

## 2. Experimental procedure

### 2.1 Characterization

X-ray diffraction (XRD) patterns were recorded by a Philips-X'PertPro, X-ray diffractometer using Ni-filtered Cu K $\alpha$  radiation at scan range of  $10 < 2\theta < 80$ . Scanning electron microscopy (SEM) images were obtained on LEO-1455VP equipped with an energy dispersive X-ray spectroscopy. The energy dispersive spectrometry (EDX) analysis was studied by XL30, Philips microscope. UV-vis diffuse reflectance spectroscopy analysis was carried out using Shimadzu UV-vis scanning spectrometer.

### 2.2 Synthesis of TiO<sub>2</sub> precursor sol

Tetrabutylorthotitanate, ethanol, thiourea, hydrochloric acid, and acetylacetone were purchased from Merck Company and used without further purification. In a typical procedure, tetrabutylorthotitanate (2.5 mL) was dissolved in 10 mL of ethanol. Subsequently, acetylacetone (2.5 mL) was added to the solution under vigorous stirring at room temperature. Acetylacetone was applied to prevent oxidation of tetrabutylorthotitanate [12]. Afterwards, during dissolution, 2 mL of distilled water was added to above solution and hydrochloric acid as a pH controller agent was added to the solution under stirring at room temperature to reach pH value 1.8. Furthermore, thiourea (0.25 g) was added to above solution to functionalized TiO<sub>2</sub> in order to absorption in visible region and was kept stirring for 2 h to forma viscous sol.

### 2.3. Deposition of tetrabutylorthotitanate thin films

For deposition of TiO<sub>2</sub> sol on the glass balls, the glasses balls substrates were dipped in the tetrabutylorthotitanate sol for 10 min and pulled out slow and then was allowed to dry at room temperature naturally. Moreover, the thin film of tetrabutylorthotitanate was further dried in an oven at 60 °C for 4 h and 500 °C for 1 h in order to remove ethanol and to convert rutile form of TiO<sub>2</sub> to its anatase form and obtain crystalline titania films. After thermal treatments, the glass balls were allowed to cool to room temperature naturally; the produces formed were washed with distilled water several times and dried under vacuum at 120 °C.

### 2.4. Photocatalytic studies

In order to photo-degradation of basic yellow 28 using TiO<sub>2</sub> thin film as photocatalyst, the glass balls fixed-bed reactor system consists of 3 glass tube of dimensions 7.5 mm diameter  $\times$  200 mm length was used. The NSTO photo-catalyst (4.2 g) was coated on glass balls as substrate. The NSTO were loaded into

the reactor columns. The solution of basic yellow 28 dye (100 mL, 50 ppm) was fed into the reactor column and kept in dark place for 30 min. After 30 min, the reactor was irradiated with visible light for 6 h. The samples after irradiation were separated and analyzed with UV-visible spectrophotometer (Shimadzu). The change in the concentration of dyes of the irradiated samples was monitored by UV-visible spectrometer.

### 3. Results and discussion

XRD pattern of the as-synthesized NSTO Thin film is shown in Fig. 1. The XRD patterns of the as-synthesized NSTO thin film (Fig. 1) indicate the formation of tetragonal phase of NSTO thin film (JCPDS No. 04-0477).

EDX is an x-ray technique used to identify the elemental composition of NSTO thin film (Fig. 2). Based on the Fig. 2, only Ti, O, N, and S elements are present.

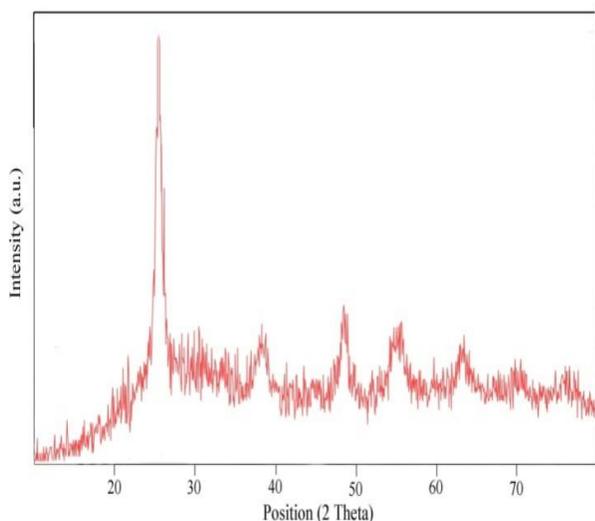


Fig. 1. XRD pattern of NSTO thin film.

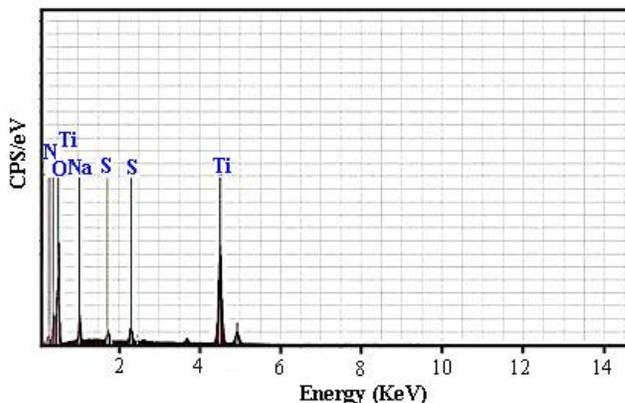


Fig. 2. EDX pattern of NSTO thin film.

The surface microstructure of the glass balls coated by NSTO thin film was investigated by scanning electron microscope (SEM). According to Fig. 3, it is seen that the products are tiny and composed of aggregated nanoparticles with spherical shapes.

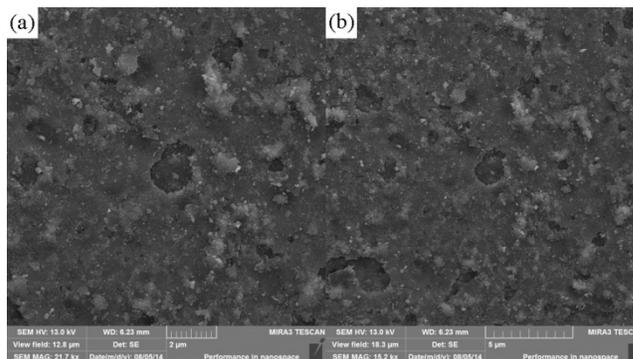
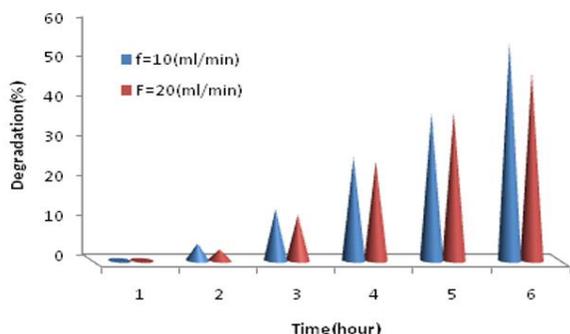


Fig. 3. (a-b) SEM images of NSTO thin film.

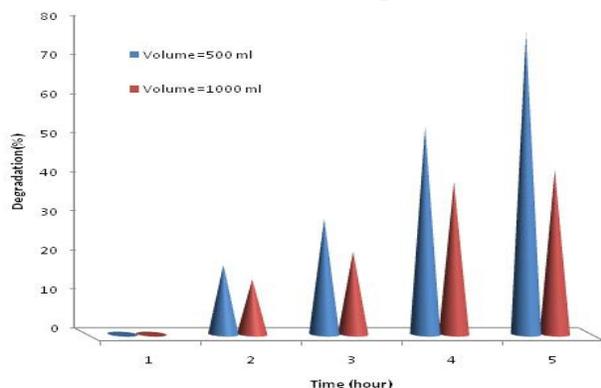
The influence of flow rate of dye solution on degradation kinetics of basic yellow 28 was investigated using different flow rate of 10 and 20 mL min<sup>-1</sup> in the presence of NSTO thin film at pH value 4.7 (natural pH) under visible light irradiation (Fig. 4). According to the Fig. 4, the degradation rate was decreased with the increase in flow rate of dye solution from 10 to 20 mL min<sup>-1</sup>

due to decrease interaction among NSTO thin film with dye solution.



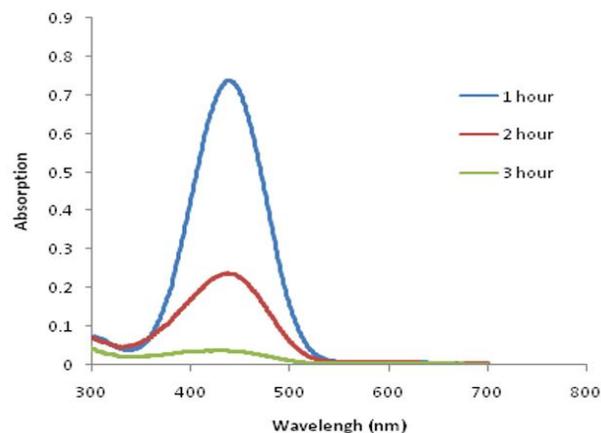
**Fig. 4.** The effect of changing flow rate 10 and 20 mL min<sup>-1</sup> on the degradation efficiency

In order to examine the effect of volume of dye solution on the decomposition rate, the number of glass tubes were increased from 3 (NSTO thin film 224.4 cm<sup>2</sup> g<sup>-1</sup>) to 7 (NSTO thin film 523.7 cm<sup>2</sup> g<sup>-1</sup>) in the constant dye concentration 50 ppm. The degradation rates for the decomposition of basic yellow 28 as a function of volume of dye solution in 500 and 1000 mL employing photocatalyst NSTO thin film (523.7 cm<sup>2</sup> g<sup>-1</sup>) are shown in Fig. 5. According to the Fig. 5, increase the volume of dye solution causes the decrease in interaction between NSTO thin film and dye solution; therefore, result in decrease decomposition rate.



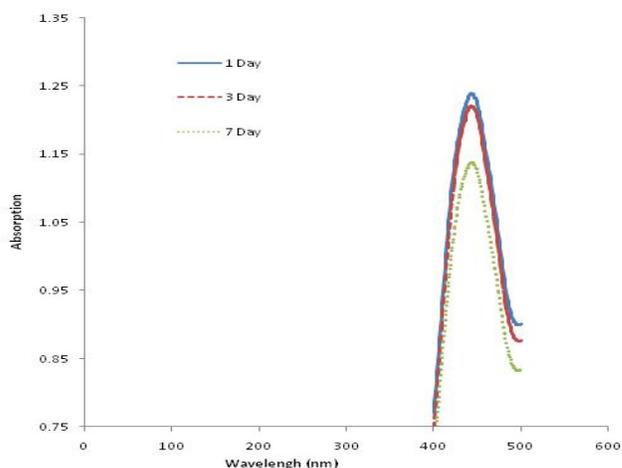
**Fig. 5.** The effect of volume of dye solution 500 and 1000 mL on the degradation efficiency

Fig. 6 shows the effect of all conditions on the decomposition rate. Based on the Fig. 6, decomposition rate is about 100 %.



**Fig. 6.** The degradation efficiency of basic yellow 28 in optimum conditions under visible light irradiation.

In order to show the effect of NSTO thin film on the decomposition rate, one experiment was performed without NSTO thin film (Fig. 7). From the Fig. 7, it is clear that in the absence of NSTO thin film as a photocatalyst, almost negligible decolorization is observed.



**Fig. 7.** The degradation efficiency of basic yellow 28 in optimum conditions in the absence of NSTO thin film.

#### 4. Conclusion

In summary, to investigate photocatalytic degradation of the basic yellow 28 dye under visible light, the glass balls fixed-bed reactor system was applied by N-S doped anatase thin films TiO<sub>2</sub> (NSTO). Besides, several factors such as volume of dye solution and exit flow rate of dye solution that influence the photoelectrocatalytic decomposition of basic yellow 28 under visible light irradiation have been studied. Thiourea was used as dopant to red shift the absorption edge of TiO<sub>2</sub> to a visible-light region.

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