

Research Journal of Pharmaceutical, Biological and Chemical Sciences

Nitrogen and Sulphur Doped TiO₂ for Photodegradation of Phenol under visible light.

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ABSTRACT

Synthesis of visible light-active photocatalyst by doping titanium dioxide with nitrogen and Sulphur was investigated. For the preparation of modified photocatalyst, solgel method was followed using precursors namely titanium isopropoxide, acetylacetone and ammonium nitrate. Dopant concentration of 0.75% and calcination temperature of 600°C were fixed in the surface modification of titania. The characterization of all doping combinations was done by FTIR, XRD and FESEM that confirmed existence of dopants, presence of anatase phase and finer grain size of particles correspondingly. Photocatalytic activity of the prepared samples was evaluated by testing with phenol under domestic illumination lamp as a visible-light source. The performance of the codoped photocatalyst (N-S-TiO₂) was found to be efficient as it resulted in 90% degradation of phenol over three hours of irradiation time.

Keywords: Photocatalytic Degradation, Codoping, N-S-TiO₂, Visible Light-active Photocatalyst

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INTRODUCTION

The presence of harmful and hazardous pollutants in industrial wastewater results in severe environmental and health problems. Several physicochemical and biological methods are used to remove the pollutants. Each method has its own advantages and disadvantages. In wastewater treatment, especially the organic bond is hard to decompose. However, photocatalytic degradation is one of the promising technique to break the organic bond in wastewater [1]. The most commonly used photocatalyst is TiO_2 as it is stable, nontoxic and inexpensive [2-4]. Since TiO_2 is active only under UV radiation, the photocatalytic degradation process becomes expensive. Hence it is necessary to find suitable methods to make TiO_2 active under visible light. Some of the researchers have reported about doping of TiO_2 with nonmetals such as N, S, F and B, etc., so as to enhance the suitability of photocatalytic degradation under visible light [5-7]. In this study, doping and codoping of N and S were considered due to its adaptability to develop low-cost photocatalyst by solgel method. The effect of adding different dopants was studied. XRD, FTIR and FESEM were used for characterization of the synthesized photocatalysts. Finally, the modified photocatalysts was tested for its effectiveness by carrying out photodegradation of phenol with compact fluorescent lamp as the source of ordinary visible light.

MATERIALS AND METHOD

Synthesis of Photocatalyst. All the chemicals were bought from Merck and were utilized without further purification. The precursor used for TiO_2 source was titanium isopropoxide and the sources of dopants, namely nitrogen and sulphur were ammonium nitrate and thiourea respectively. The dopant precursors in required quantities (to get 0.75% concentration) were mixed with calculated quantities of distilled water and acetic acid with a constant stirring and labeled as solution A. Similarly Solution B was prepared by dissolving required quantities of titanium isopropoxide in ethanol. The sol was prepared by mixing Solution A dropwise with solution B with continuous stirring for 60 minutes. After getting a gel, it was kept for aging process for a whole day. The sol was then dried at 110°C for 360 min followed by calcination process at 600°C to get doped TiO_2 in form of powder [9].

Characterization. The crystal size of doped TiO_2 was characterized by using X-ray Diffraction (XRD, Rigaku, Ultime IV) with $\text{Cu K}\alpha$ radiation at a scanning rate of $6^\circ/\text{min}$ in a 2θ range of 20° - 80° . The average crystallite size was determined from XRD data by using Scherrer equation. Fourier Transform Infrared Spectroscopy (FTIR, Perkin Elmer, Spectrum One) was used to detect the bond existence in the doped TiO_2 . Field Emission Scanning Electron Microscopy (FESEM, model DSM 982 Gemini Supra 40VP) was used to check the surface morphology and the size of the synthesized photocatalysts.

Photocatalytic Degradation. Photocatalytic activity of the modified photocatalyst was evaluated using a standard batch photocatalytic experiment using phenol as a model pollutant. A 50 ml of 10 ppm phenol solution was taken in a beaker. For the first 30 minutes, the solution was stirred in dark magnetically with the photocatalyst in order to achieve adsorption desorption equilibrium state. Later the lamp kept above the beaker was turned on to start the photodegradation. A domestic illumination (compact fluorescent) lamp was used as a visible light source (24 W Tornado Energy Saver) emitting at an average rate of 2.62 W/m^2 (equivalent to green light @ 555 nm). The samples were collected at an interval of 30 minutes and centrifuged at 10000 rpm for 10 minutes to get clear supernatant solution which was analyzed for the residual concentration of phenol using UV-Visible Spectrometer (Shimadzu UV-9000) at 270 nm [10].

RESULT AND DISCUSSION

FTIR. Figure 1 shows the FTIR spectra of the modified photo catalysts prepared. The peak detected at 1217 cm^{-1} for S- TiO_2 and N-S- TiO_2 was assigned to surface-adsorbed SO_4^{2-} . According to Periyat *et al.*, [11] presence of sulphur was exhibited in the band range of 1250 cm^{-1} to 1000 cm^{-1} . Whereas, the absorption peaks at 1736 cm^{-1} corresponded to acetic acid and remaining organic material in all samples which came from synthesis step [12]. For all band below 1000 cm^{-1} indicated as titania crystal lattice vibration [13]. The band gap between 3100 - 3500 cm^{-1} represented the hydroxyl group as observed in sample N- TiO_2 and N-S- TiO_2 [14] which play important role in capturing photo-induced holes and form hydroxyl radical during photodegradation.

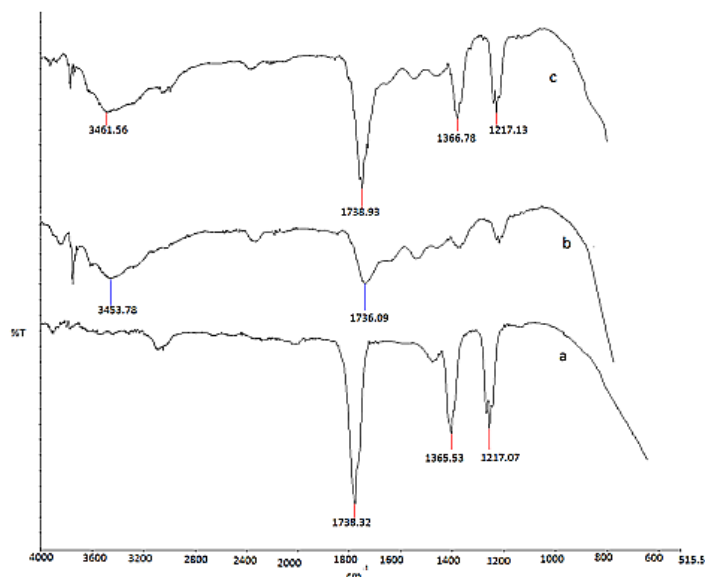


Figure 1. FTIR spectra for (a) S-TiO₂ (b) N-TiO₂ (c) N-S-TiO₂

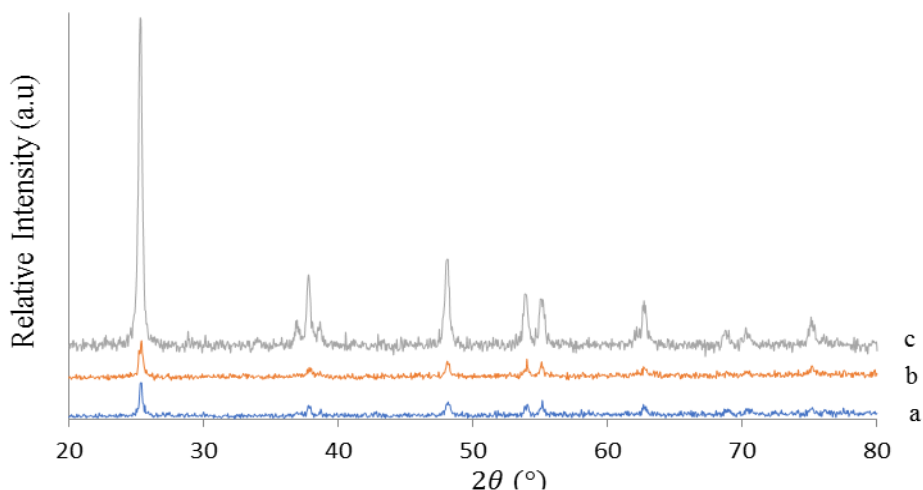


Figure 2. XRD pattern for (a) S-TiO₂ (b) N-TiO₂ (c) N-S-TiO₂

XRD. The XRD pattern for all the three synthesized photocatalyst samples was given in Figure 2. For all the samples of N-TiO₂, S-TiO₂ and N-S-TiO₂ photocatalyst, a characteristic peak ($2\theta = 25.28^\circ$) assigned to anatase phase (101) was observed [15]. The brookite and rutile phases were not found in the photocatalyst. Furthermore, no other elements are present in the graph because the nitrogen and sulphur dispersed uniformly in the anatase phase [16,17]. Using Scherrer Equation, the theoretical average crystal size was calculated and shown in Table 1.

Table 1. The Average Crystallite Size

Photocatalyst	Size, D (nm)
S-TiO ₂	0.212
N-TiO ₂	0.233
N-S-TiO ₂	0.259

FESEM. The FESEM images of S-TiO₂, N-TiO₂ and N-S-TiO₂ were presented in Figure 3 which revealed the synthesized particles were found to be finer size and spherical shape. However, some agglomeration of particles was observed that was possibly by merging of particles due to high temperature during calcinations step.

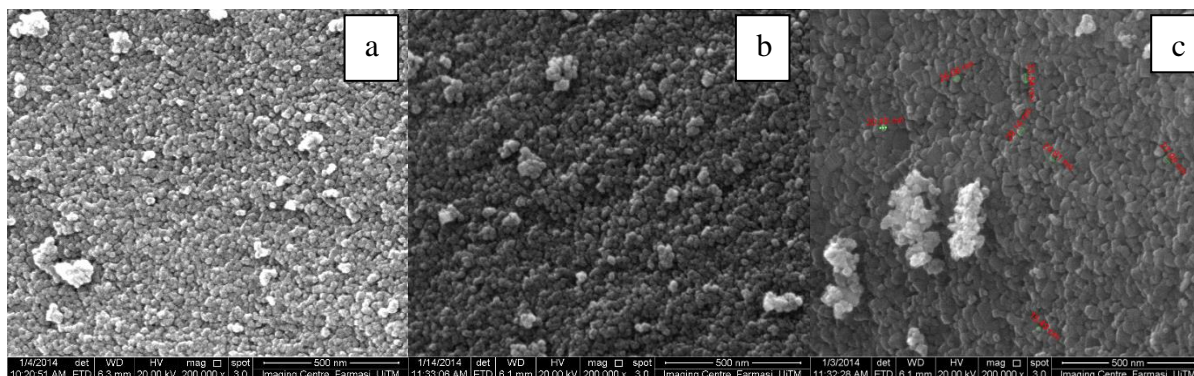


Figure 3. FESEM image for (a) S-TiO₂, (b) N-TiO₂, (c) N S-TiO₂

Photocatalytic Activity. The photocatalytic activity was evaluated in terms of removal efficiency of phenol under the illumination of compact fluorescent lamp as the source of visible light. All the experiments were carried out in a batch mode for a period of 180 minutes of irradiation time with 10 ppm initial concentration of phenol solution and a relative performance of the photocatalysts was compared [18-20]. The photodegradation profiles obtained were shown in Figure 4. The maximum photocatalytic activity of 90% was observed for N-S-TiO₂ that might be possibly due to the mixed effect of anatase phase structure formed, elements that have doped and particle size of the photocatalyst. XRD shows strong anatase peaks which exemplify a strong interaction of all the dopants with TiO₂ surfaces, resulting in higher photocatalytic degradation. The photocatalytic reaction was also influenced by the particle size. Finer the size, more efficient is the photocatalytic performance that was well supported by the FESEM results. As discussed in FTIR results, the presence of hydroxyl group in the photocatalyst also improved photocatalytic activity. Similar results were reported by Krishnan et al (2014) with N-C-TiO₂.

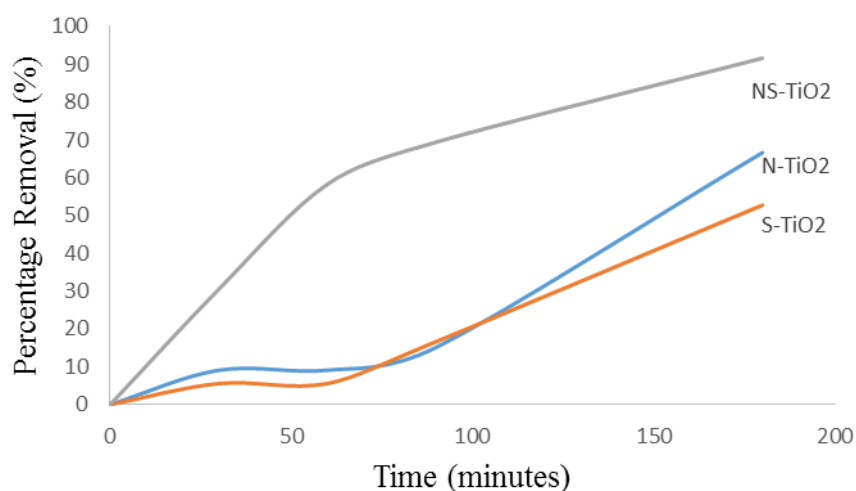


Figure 4. Photocatalytic degradation of phenol

CONCLUSION

The doped N-TiO₂, S-TiO₂ and codoped N-S-TiO₂ photocatalyst with a dopant concentration of 0.75% were successfully prepared using sol-gel method at room temperature and calcined at 600°C. The presence of dopants were witnessed by FTIR analysis. The anatase phase transformation of TiO₂ was supported by XRD analysis. FE-SEM analysis confirmed finer size of the photocatalyst. Both doped (N-TiO₂ and S-TiO₂) and codoped titania (N-S-TiO₂) were very effective in degrading phenol under visible light, as a consequence of anatase phase structure and fine-structure morphology of the photocatalyst. The codoped photocatalyst (N-S-TiO₂) was found to be a potential visible light-active photocatalyst for the phenolic

wastewater treatment, as the standard photodegradation tests with phenol exhibited a maximum removal efficiency of 90% in 180 minutes of irradiation time.

ACKNOWLEDGEMENT

Authors are very thankful to the Department of Chemical Engineering, SSN college of Engineering for providing the facilities to carry out this research work.

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