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Photocatalytic Degradation of Basic Fuchsine Dye Using 1:3, 1:4 Sulphur Doped Titanium Dioxide Catalyst

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Abstract

Preparation of Titanium Dioxide doped with Sulphur photocatalyst along with Nitrogen using Thiourea and Titanium Dioxide was performed in this work. The photocatalysts were prepared in the ratios of 1:3 and 1:4 with the former materials and the temperature effects were found out by varying the temperature of the photocatalysts prepared. The prepared photocatalysts were experimented on the staining dye named Basic Fuchsine for photodegradation using artificial light. The photodegradation was performed on the dye with various concentrations of the prepared photocatalysts. The enhanced visible light activity of the photocatalysts on the dye was observed. Analysis using pH changes, Spectral studies such as X-Ray Diffraction studies, Scanning electron microscopic studies, Energy dispersive X-Ray analysis, Infrared analysis, UV-Vis spectral studies were made. Enhanced efficiency of the photocatalysts was observed on the Basic Fuchsine dye with decrease in the absorbance value of the degraded dye.
Keywords: Titanium Dioxide; Sulphur; Photocatalysts; Nitrogen; Thiourea; Basic Fuchsine.

1. INTRODUCTION

Negative effects of pollutants on the aquatic system have always had great carcinogenic impact on living being causing health issues, sickness and short shelf life [1]. Photocatalysis is one of the promising methods for the decomposition of pollutants. Titanium Dioxide is a known compound acts as a photocatalyst and it is used in most of the fields as per today's technologies involved. Ultraviolet light can be absorbed at the rate less than 380nm by this catalyst and it is also used in the photocatalytic organic pollutant degradation [2-4]. Titanium Dioxide is a semiconductor material investigated to have high photocatalytic activity based on the photon absorption initiation reactions [5,6]. In recent time, Titanium dioxide co-doping has been studied extensively for the production of new materials and used in spintronic applications. The unique property of Titanium dioxide has been studied physically and chemically for its elevation in refractive index, fineness in transmission of optics in the visible light region and infra red region and has more dielectric constant. The co-doped Titanium dioxide compounds have shown

paramagnetic properties, super paramagnetic properties and can have ferromagnetic behaviour [7]. The rise of the environmental crisis and energy crisis has lead to the exploration of renewable energy sources more rapidly. It is complicated to treat waste water by normal processes like biochemical processes [8] and filtrations. Titanium dioxide being a good photocatalytic conductor has a lot of consideration owing to its chemical stability, non toxicity, oxidizing power and low cost [9]. It is reported that it has potential ability for removal of pollutants from waste water and increased absorption [10]. The application of Titanium dioxide has extended towards Lithium ion batteries, Dye sensitized solar cells and in electronics [11-13]. Waterways get polluted easily due to many external factors and the purification of water has gained importance in all the fields. Dyes are used in many fields including industries, medical field etc. but the dye waste water release is harmful for the aquatic environment and the marine land. They can be carcinogenic and can cause irritation physically and health issues internally. Subsequently, effective dye removal techniques have to be found. Biological treatment is one of the techniques where colored effluents can be removed [14]. Photocatalytic degradation is one of the methods [15] where dyes are degraded using light with the usage of photocatalyst to fasten the process. The use of light energy has become efficient as a part of modern science and technology and can be used for photocatalytic degradation of many dyes [16]. Titanium dioxide has a wide band gap of 3.2 eV and requires UV light for photoactivity. The doping of non metals increased its optical response to shift from UV to visible spectral rate [17]. In this work, we report the Basic Fuchsine dye degradation with the photocatalyst in the ratio of 1:3 and1:4 and the photocatalytic preparation and characterization and the reactivity of co-doped photocatalysts were evaluated with irradiation.

2. Material and methods

2.1 Supplies Used

Basic Fuchsine dye (Sigma Aldrich), Commercial Titanium dioxide (Spectrum Chemicals), aqueous solution of thiourea (Spectrum Chemicals) were used as materials without further refinement. Double distilled water was obtained from the purity distiller. Solvents like acetone, ethanol and hydrochloric acid were used for washing purposes. Steam Bath, muffle furnace. KBr pellets for IR were used as ancillaries.

2.2 Synthesis of Sulphur doped Titanium Dioxide Photocatalyst

Sulphur doped Titanium dioxide photocatalyst was synthesized using thiourea and powdered Titanium dioxide. Different ratios of thiourea and Titanium dioxide were taken in suitable proportions and the photocatalyst was synthesized previously [18]. Here, the sulphur doped Titanium dioxide taken in the ratio of 1:3 and 1:4 are discussed. The ratio was varied for thiourea

keeping Titanium dioxide constant. Double distilled water was taken freshly and used for dissolving both the components. The mixture was kept in the dark for 24 hours and steamed using steam bath and evaporated and scrapped out of the container. The sample was transferred to a silica crucible and heated in a muffle furnace at different temperature rates for about 400,500 and 600^0 C. The photocatalyst prepared was experimented with different concentrations on the Basic Fuchsine dye.

2.3 Photodegradation Process

The Basic Fuchsine dye as aqueous solution was taken in a beaker and the sulphur doped Titanium dioxide photocatalyst was experimented in different concentrations such as 0.01g, 0.02g, 0.03g on the dye. Initial value of absorbance (I_0) was taken for the dye before photodegradation. Artificial light of about 200 Watts was used for the photodegradation process. The photodegraded samples were taken out and analyzed by the Ultraviolet spectroscopy for every 30 minutes interval for 3 hours. The value was determined by the UV spectroscopic technique [19].

3. RESULTS AND DISCUSSION

3.1 Determination of pH of the Basic Fuchsine Dye before and after photodegradation

Before photodegradation - 8.2
After photodegradation - 8.2-8.9

The initial pH before dye degradation was 8.2 and it varied till 8.9 when added photocatalyst and subjected to photodegradation.

3.2 Tables and Figures

Table 1: Dye samples in the dark

Time (hours)	Wavelength (nm)	Absorbance (arbitrary units)
0 - 3	537.2	0.956

The dye sample was degraded in the dark and the initial wavelength was 537.2 and the absorbance was determined to be 0.956.

Table 2: Dye samples in the light without photocatalyst

Time (hours)	Wavelength (nm)	Absorbance (arbitrary units)
0-3	537.2	0.956-0.800

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The dye samples were checked for photodegradation without the presence of photocatalyst detailed in our previous publication [20].

Table 3: Dye samples in the light with 0.01g, 1:3, 400°C S,N-TiO_2 photocatalyst

Time (hours)	**Wavelength (nm)**	**Absorbance (arbitrary units)**
0	537.2	0.956
0.5		0.659
1		0.611
1.5		0.58
2		0.564
2.5		0.516
3		0.471

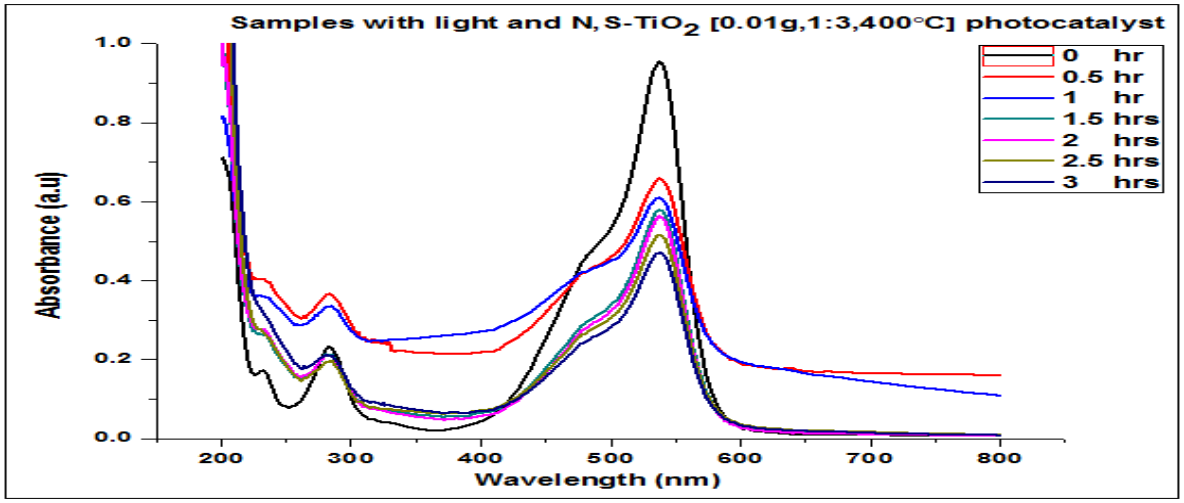

Figure 1: Ultraviolet Spectroscopic images of the dye samples depicting Table 3.

Table 4: Dye samples in the light with 0.01g, 1:4, 400°C S,N-TiO_2 photocatalyst

Time (hours)	Wavelength (nm)	Absorbance (arbitrary units)
0	537.2	0.956
0.5		0.692
1		0.604
1.5		0.603
2		0.563
2.5		0.484
3		0.471

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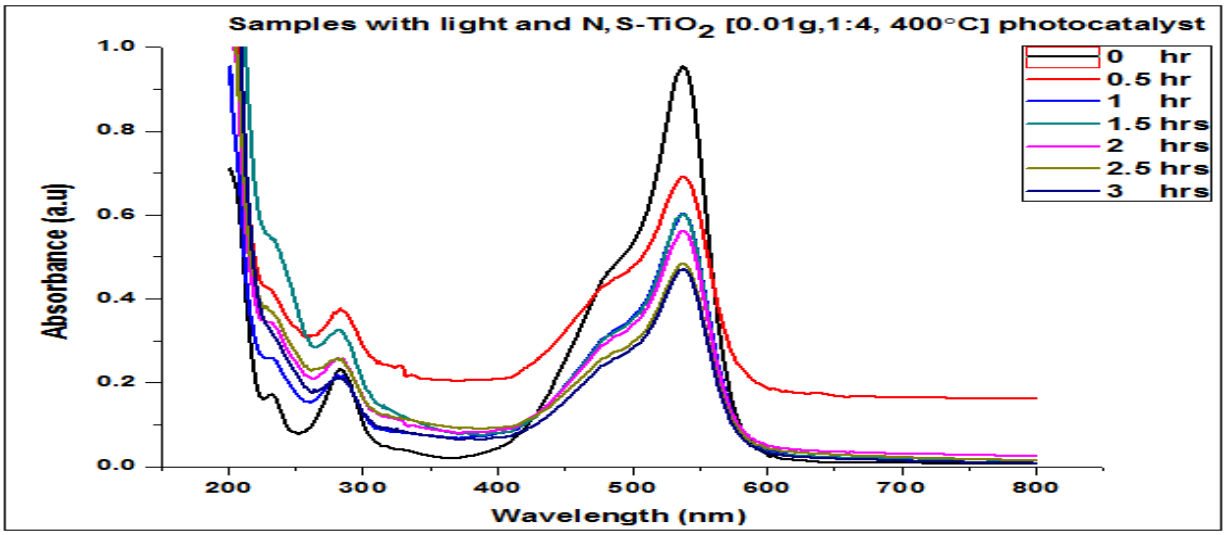

Figure 2: Ultraviolet Spectroscopic images of the dye samples depicting Table 4.

Table 5: Dye samples in the light with 0.01g, 1:3, 500°C S,N-TiO_2 photocatalyst

Time (hours)	Wavelength (nm)	Absorbance (arbitrary units)
0	537.2	0.956
0.5		0.519
1		0.46
1.5		0.451
2		0.429
2.5		0.423
3		0.395

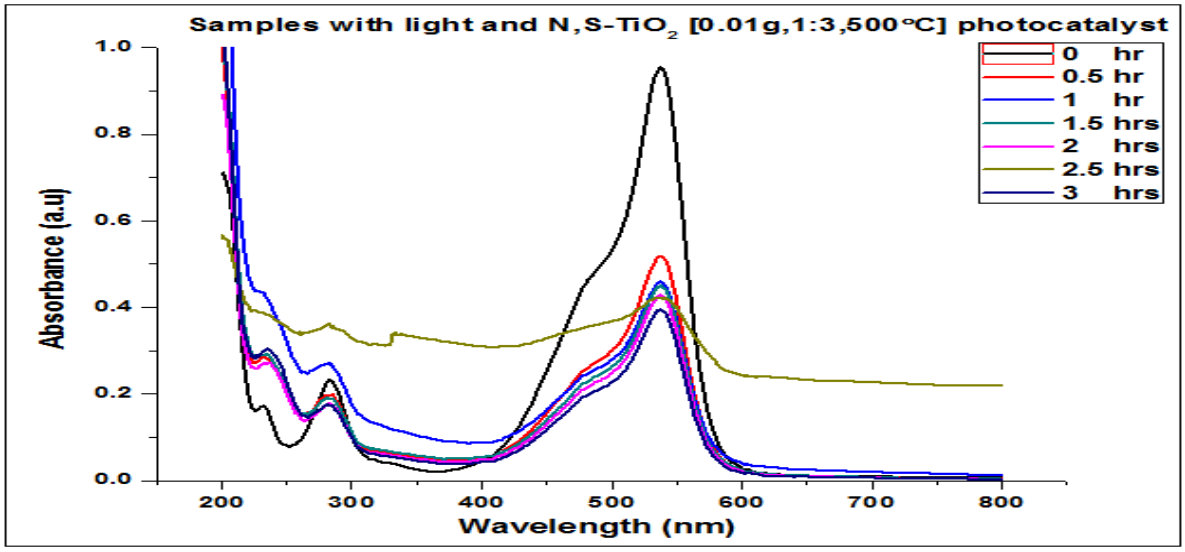

Figure 3: Ultraviolet Spectroscopic images of the dye samples depicting Table 5.

Table 6: Dye samples in the light with 0.01g, 1:3, 600°C S,N-TiO_2 photocatalyst

Time (hours)	Wavelength (nm)	Absorbance (arbitrary units)
0	537.2	0.956
0.5		0.63
1		0.624
1.5		0.556
2		0.541
2.5		0.528
3		0.426

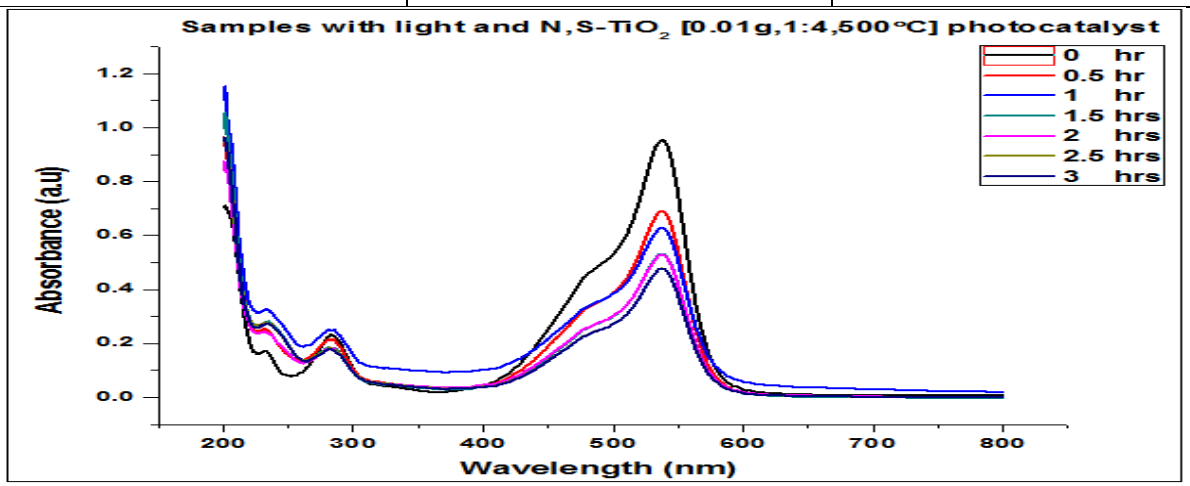

Figure 4: Ultraviolet Spectroscopic images of the dye samples depicting Table 6.

Table 7: Dye samples in the light with 0.01g, 1:3, 600°C S,N-TiO_2 photocatalyst

Time (hours)	Wavelength (nm)	Absorbance (arbitrary units)
0	537.2	0.956
0.5		0.63
1		0.624
1.5		0.556
2		0.541
2.5		0.528
3		0.426

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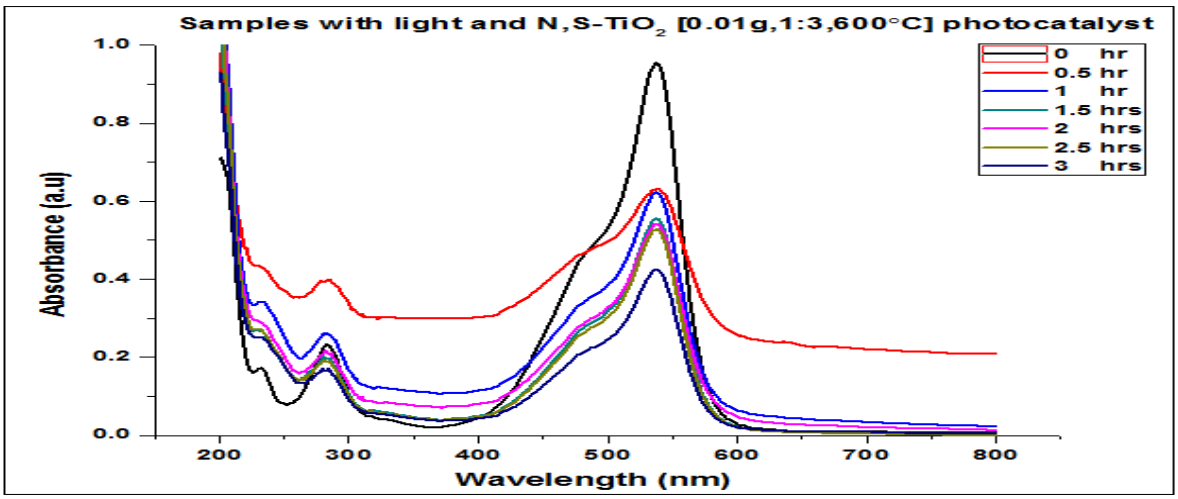

Figure 5: Ultraviolet Spectroscopic images of the dye samples depicting Table 7.

Table 8: Dye samples in the light with 0.01g, 1:4, 600°C S,N-TiO_2 photocatalyst

Time (hours)	Wavelength (nm)	Absorbance (arbitrary units)
0	537.2	0.956
0.5		0.613
1		0.604
1.5		0.548
2		0.53
2.5		0.528
3		0.508

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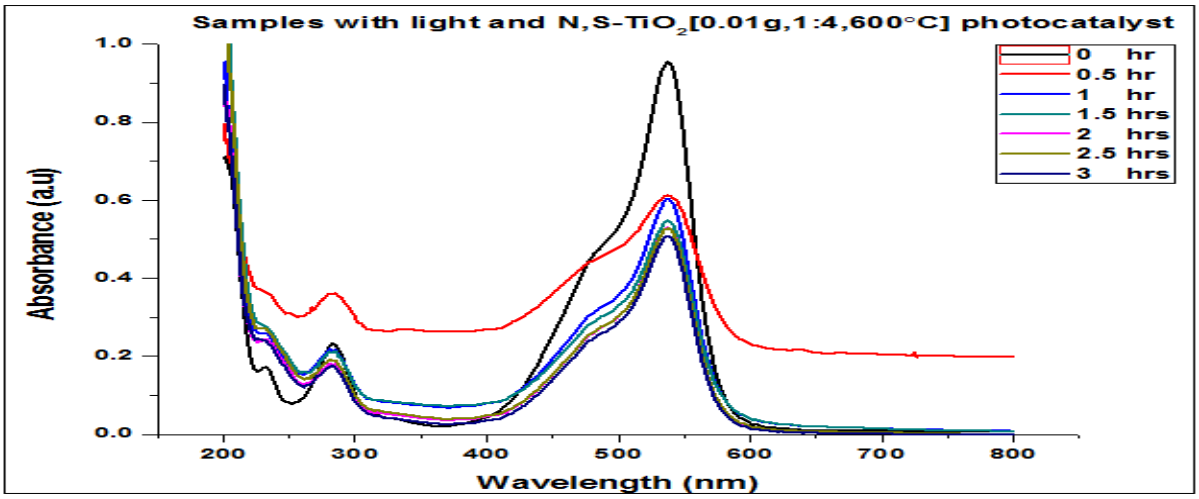

Figure 6: Ultraviolet Spectroscopic images of the dye samples depicting Table 8.

Table 9: Dye samples in the light with 0.02g, 1:3, 400°C S,N-TiO_2 photocatalyst

Time (hours)	Wavelength (nm)	Absorbance (arbitrary units)
0	537.2	0.956
0.5		0.758
1		0.62
1.5		0.616
2		0.567
2.5		0.545
3		0.488

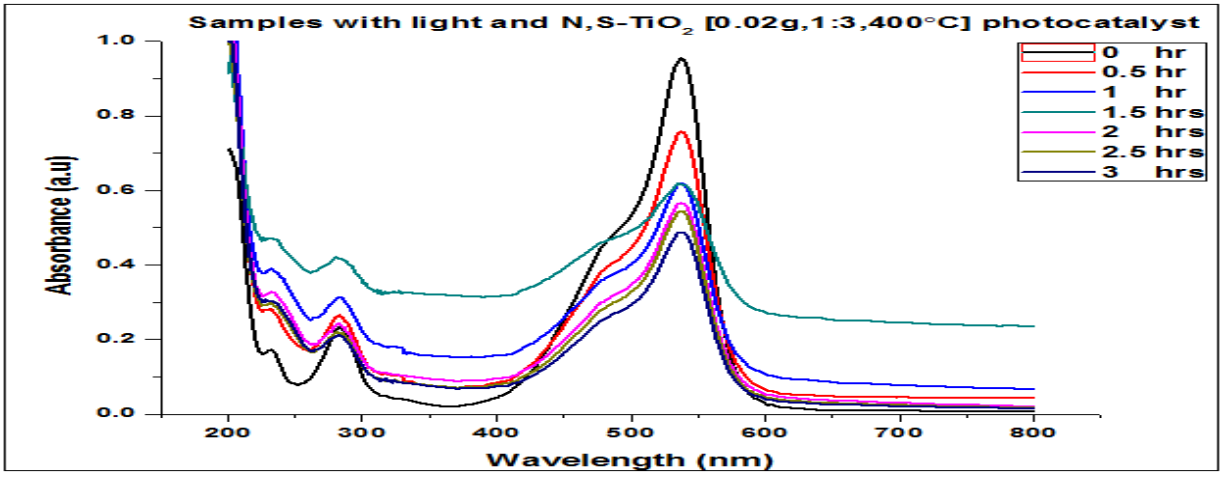

Figure 7: Ultraviolet Spectroscopic images of the dye samples depicting Table 9.

Table 10: Dye samples in the light with 0.02g, 1:4, 400°C S,N-TiO_2 photocatalyst

Time (hours)	Wavelength (nm)	Absorbance (arbitrary units)

0	537.2	0.956
0.5		0.583
1		0.524
1.5		0.463
2		0.461
2.5		0.353
3		0.344

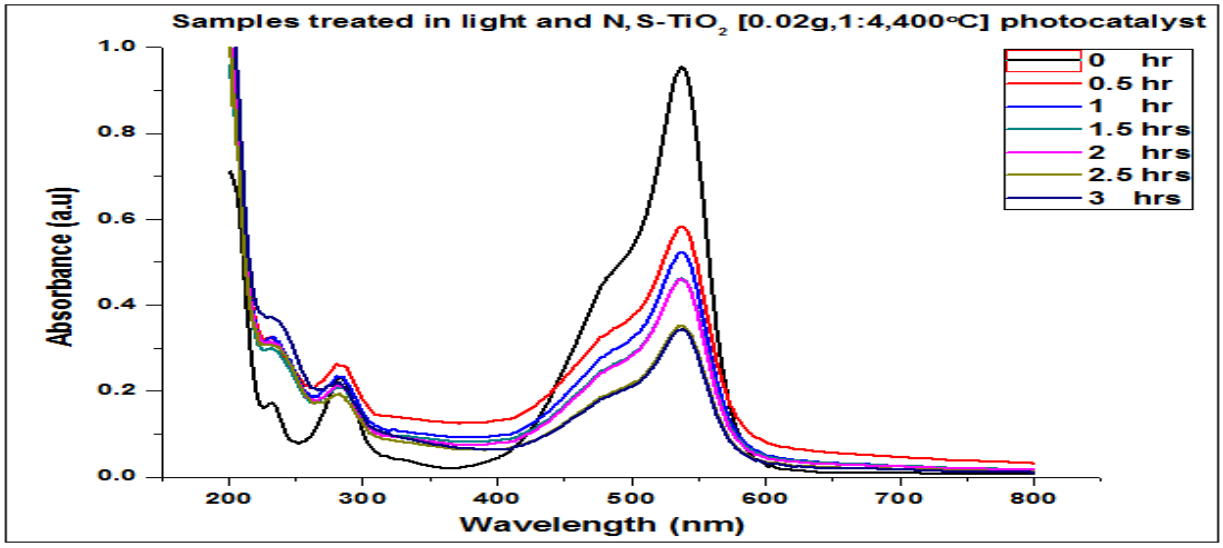

Figure 8: Ultraviolet Spectroscopic images of the dye samples depicting Table 10.

Table 11: Dye samples in the light with 0.02g, 1:3, 500°C S,N-TiO_2 photocatalyst

Time (hours)	Wavelength (nm)	Absorbance (arbitrary units)
0	537.2	0.956
0.5		0.688
1		0.581
1.5		0.556
2		0.546
2.5		0.541
3		0.474

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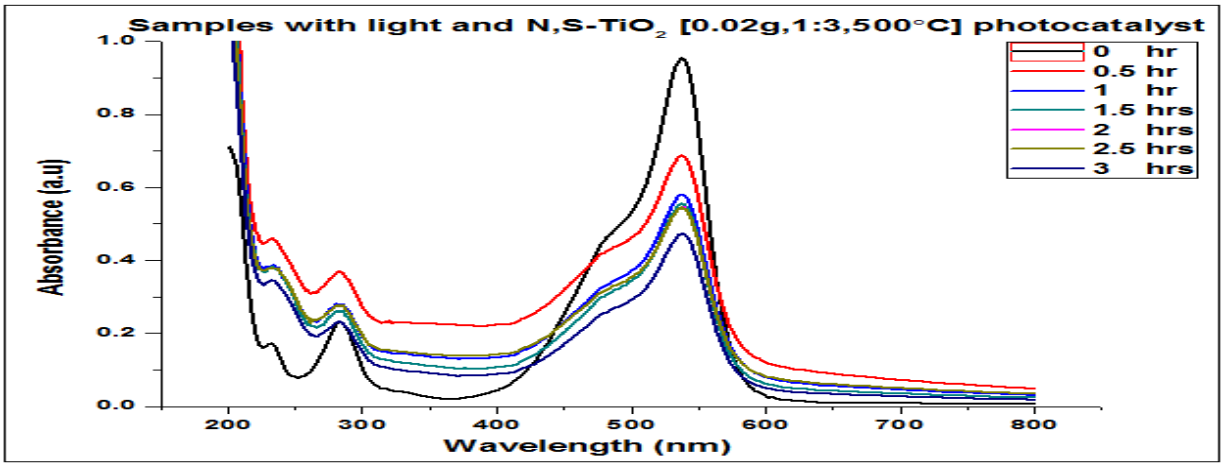

Figure 9: Ultraviolet Spectroscopic images of the dye samples depicting Table 11.

Table 12: Dye samples in the light with 0.02g, 1:4, 500°C S,N-TiO_2 photocatalyst

Time (hours)	Wavelength (nm)	Absorbance (arbitrary units)
0	537.2	0.956
0.5		0.693
1		0.655
1.5		0.624
2		0.605
2.5		0.584
3		0.582

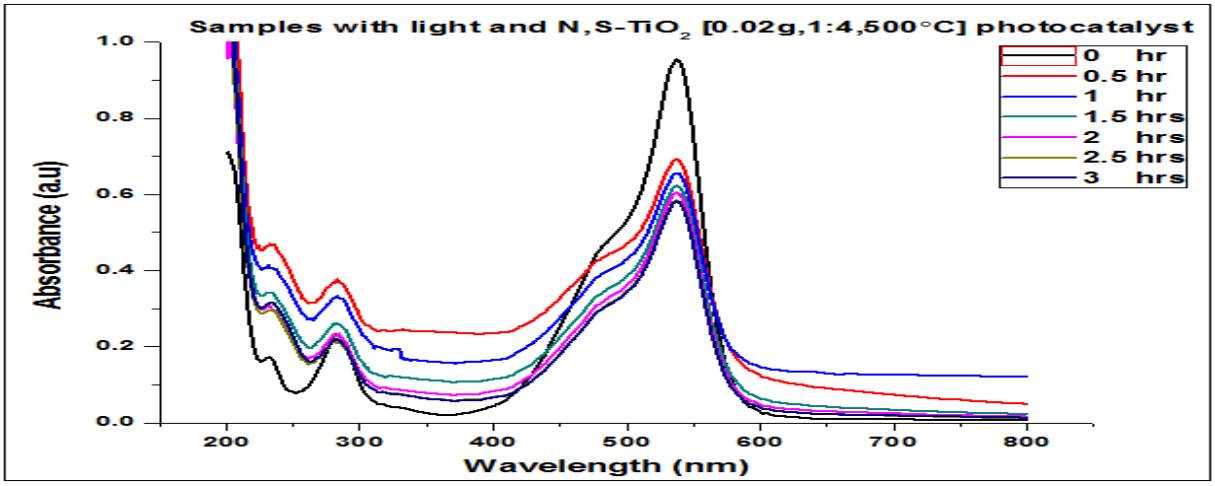

Figure 10: Ultraviolet Spectroscopic images of the dye samples depicting Table 12.

Table 13: Dye samples in the light with 0.02g, 1:3, 600°C S,N-TiO_2 photocatalyst

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Time (hours)	Wavelength (nm)	Absorbance (arbitrary units)
0	537.2	0.956
0.5		0.799
1		0.634
1.5		0.61
2		0.603
2.5		0.596
3		0.569

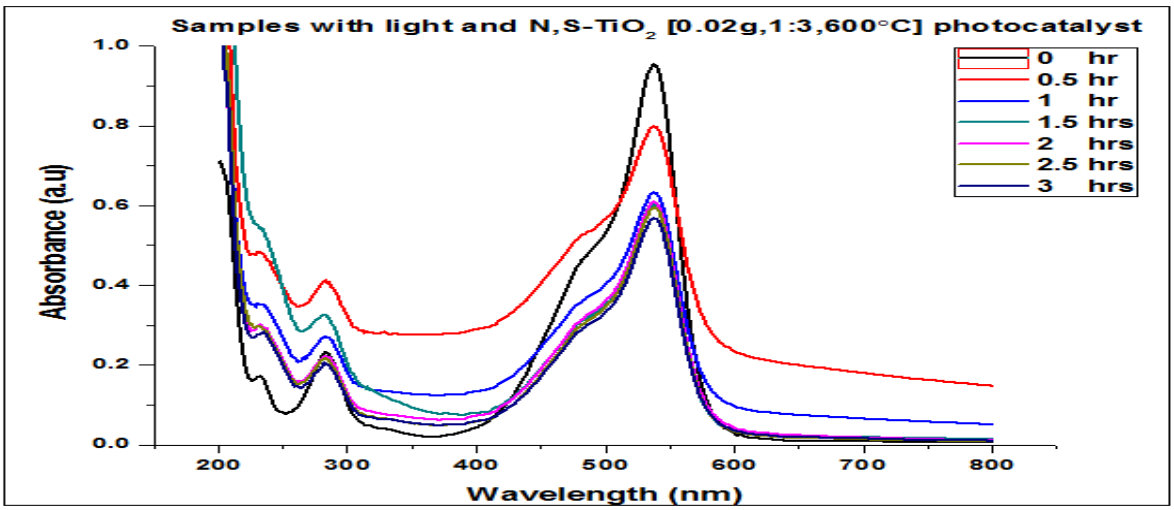

Figure 11: Ultraviolet Spectroscopic images of the dye samples depicting Table 13.

Table 14: Dye samples in the light with 0.02g, 1:4, 600°C S,N-TiO_2 photocatalyst

Time (hours)	Wavelength (nm)	Absorbance (arbitrary units)
0	537.2	0.956
0.5		0.684
1		0.671
1.5		0.66
2		0.655
2.5		0.643
3		0.637

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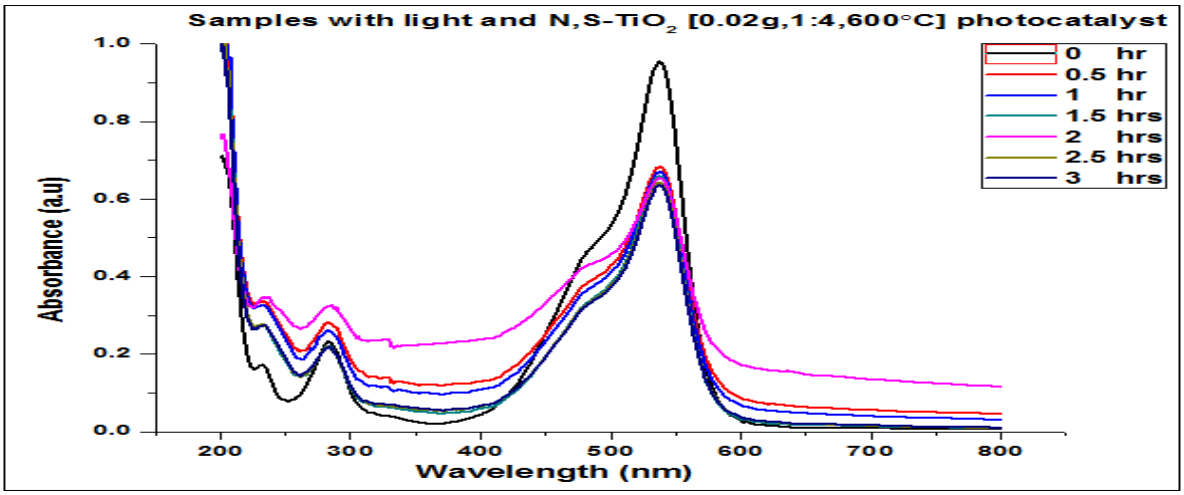

Figure 12: Ultraviolet Spectroscopic images of the dye samples depicting Table 14.

Table 15: Dye samples in the light with 0.03g, 1:3, 400°C S,N-TiO_2 photocatalyst

Time (hours)	Wavelength (nm)	Absorbance (arbitrary units)
0	537.2	0.956
0.5		0.927
1		0.853
1.5		0.833
2		0.796
2.5		0.778
3		0.686

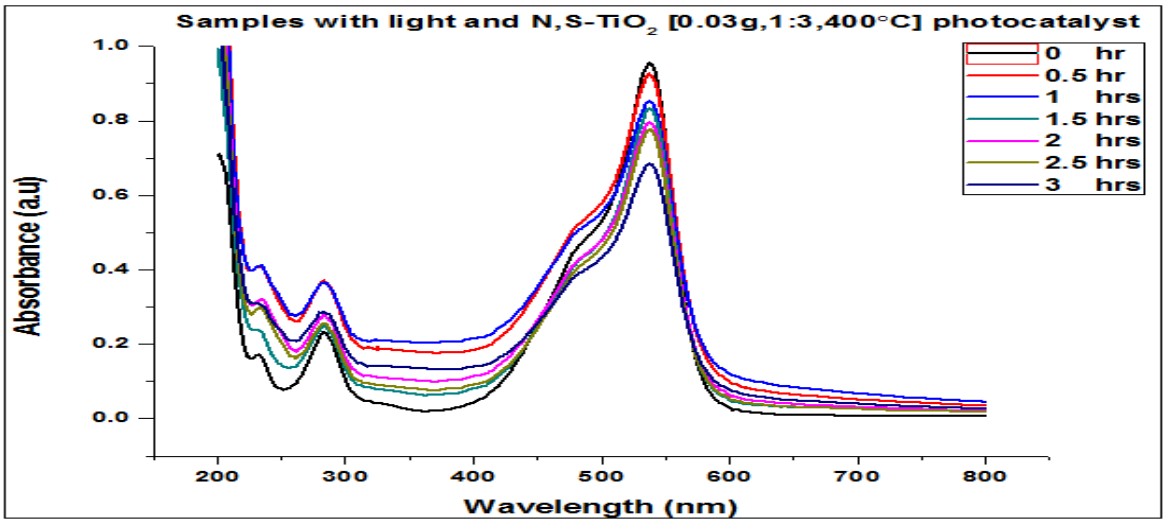

Figure 13: Ultraviolet Spectroscopic images of the dye samples depicting Table 15.

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Table 16: Dye samples in the light with 0.03g, 1:4, 400°C S,N-TiO_2 photocatalyst

Time (hours)	Wavelength (nm)	Absorbance (arbitrary units)
0	537.2	0.956
0.5		0.858
1		0.842
1.5		0.841
2		0.826
2.5		0.825
3		0.773

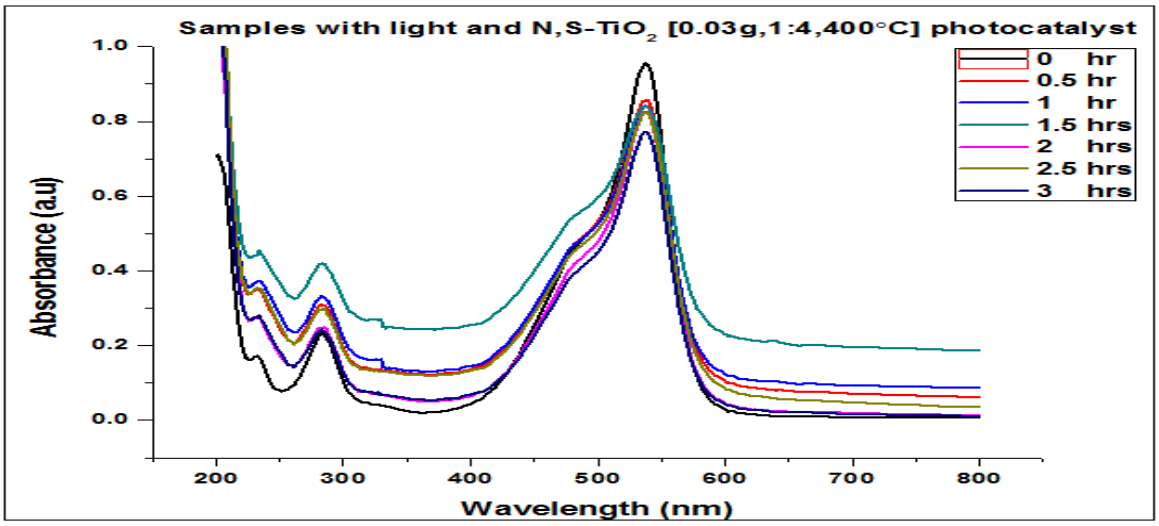

Figure 14: Ultraviolet Spectroscopic images of the dye samples depicting Table 16.

Table 17: Dye samples in the light with 0.03g, 1:3, 500°C S,N-TiO_2 photocatalyst

Time (hours)	Wavelength (nm)	Absorbance (arbitrary units)
0	537.2	0.956
0.5		0.813
1		0.790
1.5		0.746
2		0.703
2.5		0.696
3		0.689

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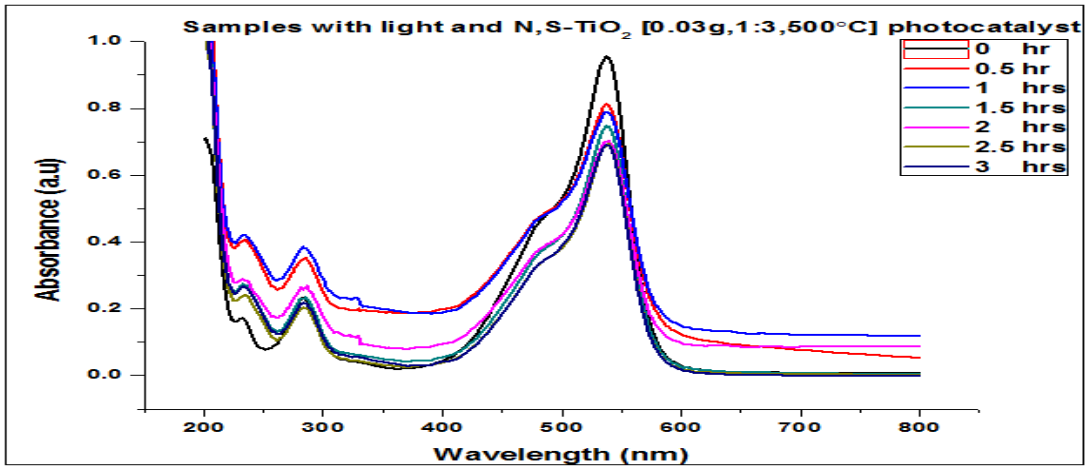

Figure 15: Ultraviolet Spectroscopic images of the dye samples depicting Table 17.

Table 18: Dye samples in the light with 0.03g, 1:4, 500°C S,N-TiO_2 photocatalyst

Time (hours)	Wavelength (nm)	Absorbance (arbitrary units)
0	537.2	0.956
0.5		0.776
1		0.748
1.5		0.744
2		0.742
2.5		0.729
3		0.719

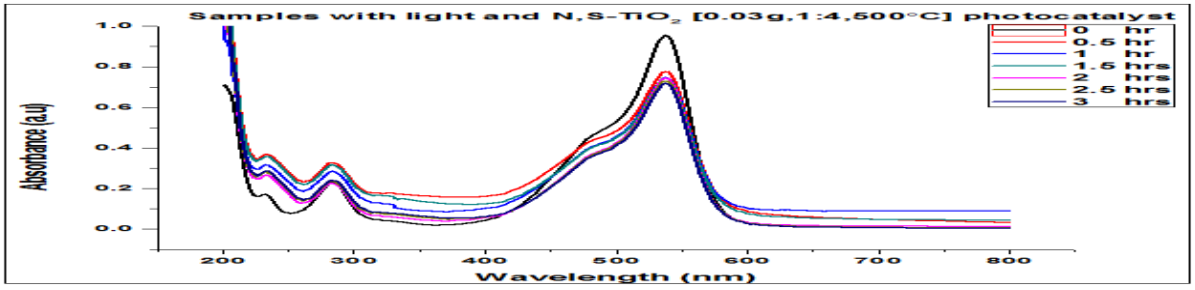

Figure 16: Ultraviolet Spectroscopic images of the dye samples depicting Table 18.

Table 19: Dye samples in the light with 0.03g, 1:3, 600°C S,N-TiO_2 photocatalyst

Time (hours)	Wavelength (nm)	Absorbance (arbitrary units)
0	537.2	0.956
0.5		0.827
1		0.766
1.5		0.727

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2		0.699
2.5		0.692
3		0.686

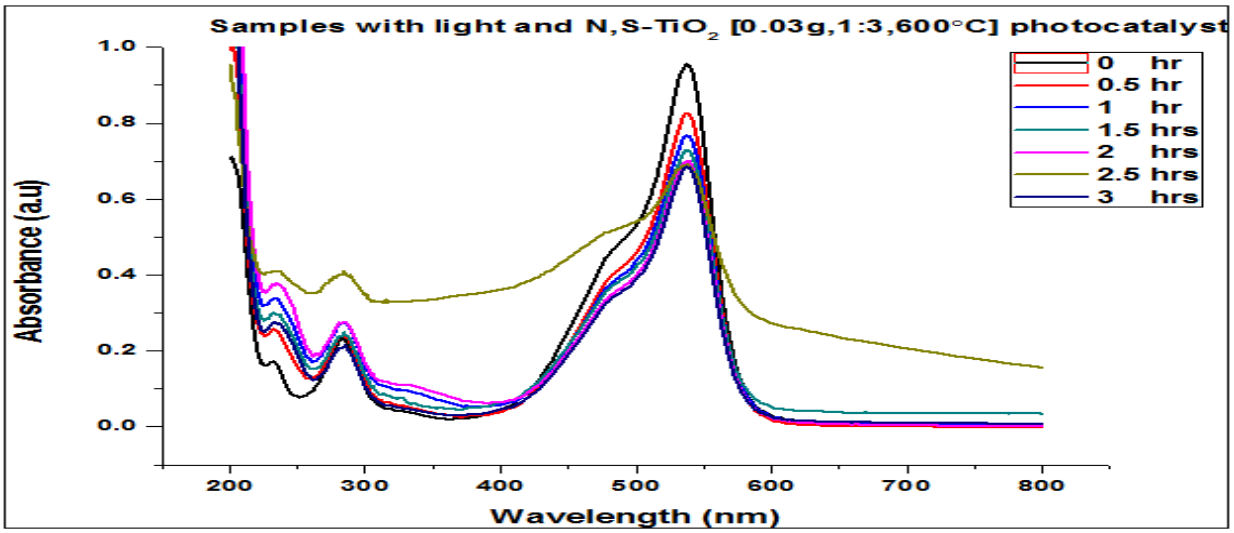

Figure 17: Ultraviolet Spectroscopic images of the dye samples depicting Table 19.

Table 20: Dye samples in the light with 0.03g, 1:4, 600°C S,N-TiO_2 photocatalyst

Time (hours)	Wavelength (nm)	Absorbance (arbitrary units)
0	537.2	0.956
0.5		0.951
1		0.874
1.5		0.858
2		0.824
2.5		0.803
3		0.798

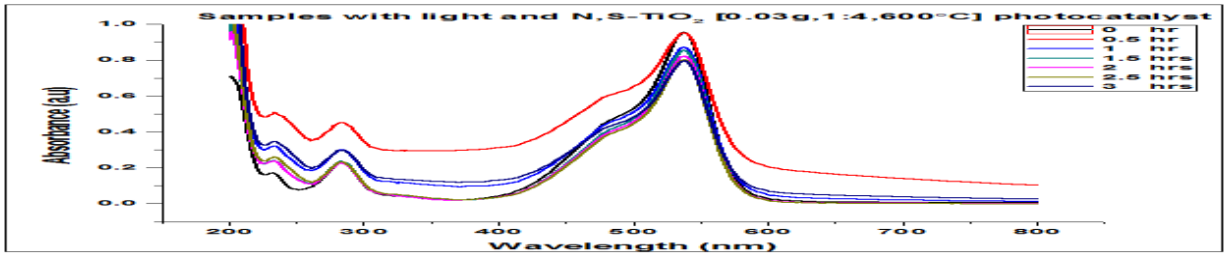

Figure 18: Ultraviolet Spectroscopic images of the dye samples depicting Table 20.

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Table 3, Figure 1 indicates that the dye has photodegraded from 0.956 to 0.471 ranges. Table 4, Figure 2 indicates that the dye has photodegraded from 0.956 to 0.471 ranges. Table 5, Figure 3 indicates that the dye has photodegraded from 0.956 to 0.395 ranges. Table 6, Figure 4 indicates that the dye has photodegraded from 0.956 to 0.477 ranges. Table 7, Figure 5 indicates that the dye has photodegraded from 0.956 to 0.426 ranges. Table 8, Figure 6 indicates that the dye has photodegraded from 0.956 to 0.508 ranges. Table 9, Figure 7 indicates that the dye has photodegraded from 0.956 to 0.488 ranges. Table 10, Figure 8 indicates that the dye has photodegraded from 0.956 to 0.344 ranges. Table 11, Figure 9 indicates that the dye has photodegraded from 0.956 to 0.474 ranges. Table 12, Figure 10 indicates that the dye has photodegraded from 0.956 to 0.582 ranges. Table 13, Figure 11 indicates that the dye has photodegraded from 0.956 to 0.569 ranges. Table 14, Figure 12 indicates that the dye has photodegraded from 0.956 to 0.637 ranges. Table 15, Figure 13 indicates that the dye has photodegraded from 0.956 to 0.686 ranges. Table 16, Figure 14 indicates that the dye has photodegraded from 0.956 to 0.773 ranges. Table 17, Figure 15 indicates that the dye has photodegraded from 0.956 to 0.689 ranges. Table 18, Figure 16 indicates that the dye has photodegraded from 0.956 to 0.719 ranges. Table 19, Figure 17 indicates that the dye has photodegraded from 0.956 to 0.686 ranges. Table 20, Figure 18 indicates that the dye has photodegraded from 0.956 to 0.798 ranges.

3.2 Infrared Spectroscopy of the S,N-TiO_2 photocatalysts

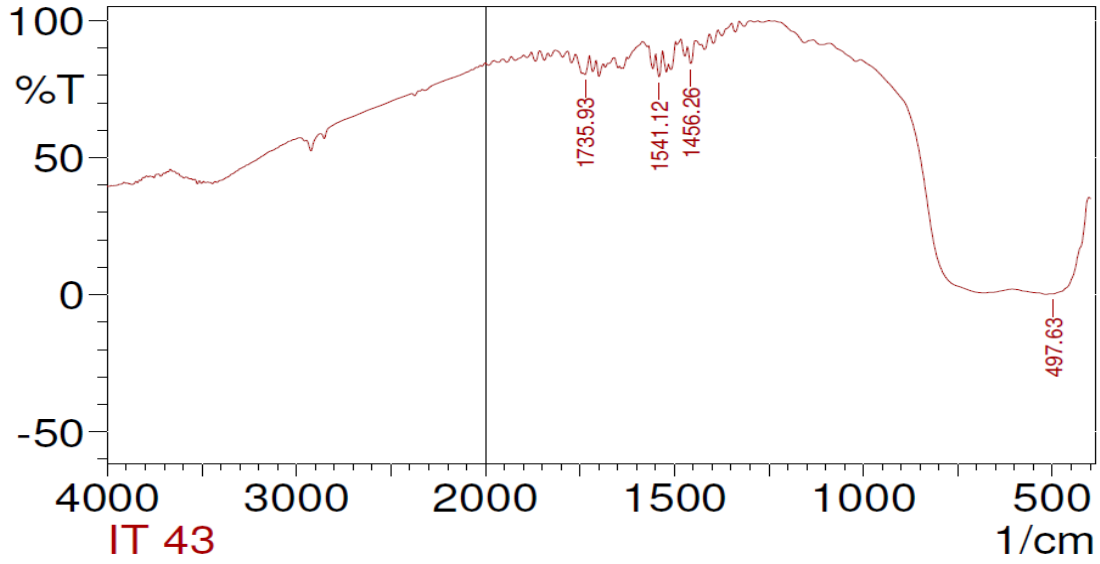

Figure 19: IR spectrum of S,N-TiO_2 (1:3,400^{0}C) photocatalyst

Table 21: IR intensities of 1:3,400^{o}C S,N-TiO_2 photocatalyst

Peak	Intensity	Correction intensity

497.63	0.328	0.739
1456.26	84.328	7.27
1541.12	79.523	8.78
1735.93	80.321	2.662

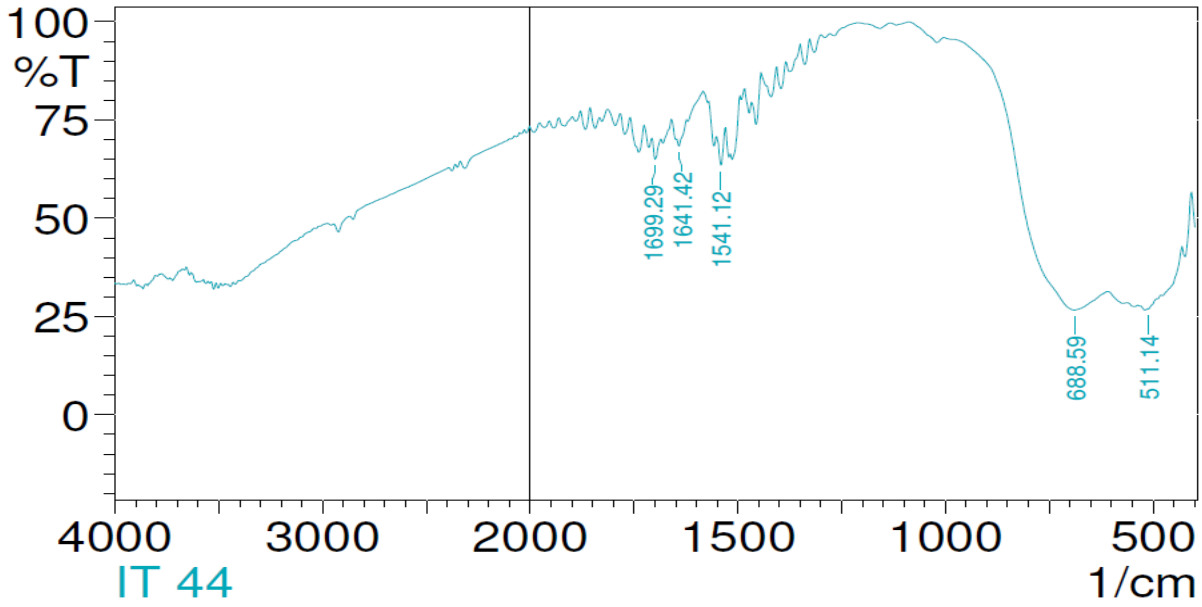

Figure 20: IR spectrum of S,N-TiO_2 (1:4,400^{0}C) photocatalyst

Table 22: IR intensities of 1:4,400^{o}C S,N-TiO_2 photocatalyst

Peak	Intensity	Correction intensity
511.14	26.927	0.257
688.59	26.677	18.394
1541.12	63.54	8.318
1641.42	68.378	3.049
1699.29	65.031	5.312

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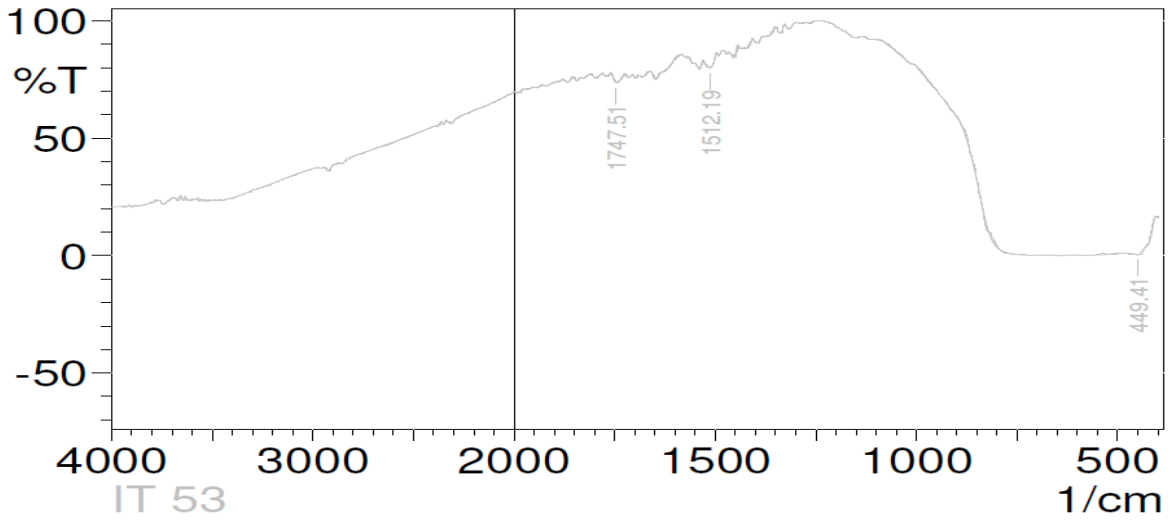

Figure 21: IR spectrum of S,N-TiO_2 (1:3,500^{0}C) photocatalyst

Table 23: IR intensities of 1:3,500^{o}C S,N-TiO_2 photocatalyst

Peak	Intensity	Correction intensity
449.41	0.309	5.965
1512.19	79.737	2.741
1747.51	73.599	4.285

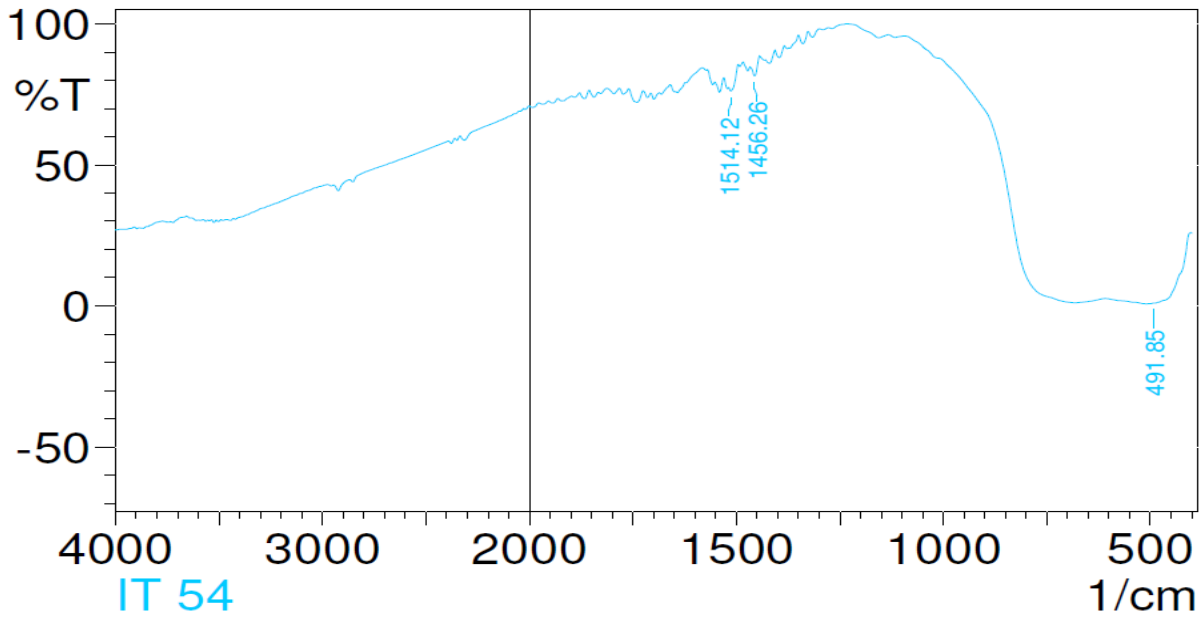

Figure 22: IR spectrum of S,N-TiO_2 (1:4,500^{0}C) photocatalyst

Table 24: IR intensities of 1:4,500^{o}C S,N-TiO_2 photocatalyst

Peak	Intensity	Correction intensity
491.85	0.943	0.532
1456.26	81.507	5.189
1514.12	76.099	2.671

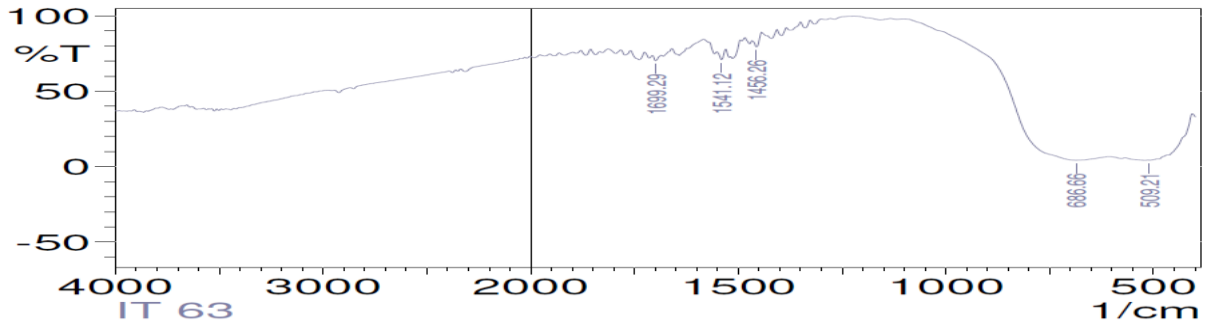

Figure 23: IR spectrum of S,N-TiO_2 (1:3,600^{0}C) photocatalyst

Table 25: IR intensities of 1:3,600^{o}C S,N-TiO_2 photocatalyst

Peak	Intensity	Correction intensity
509.21	4.257	0.412
686.66	79.328	17.617
1456.26	79.328	7.066
1541.12	70.898	6.142
1699.29	70.232	3.596

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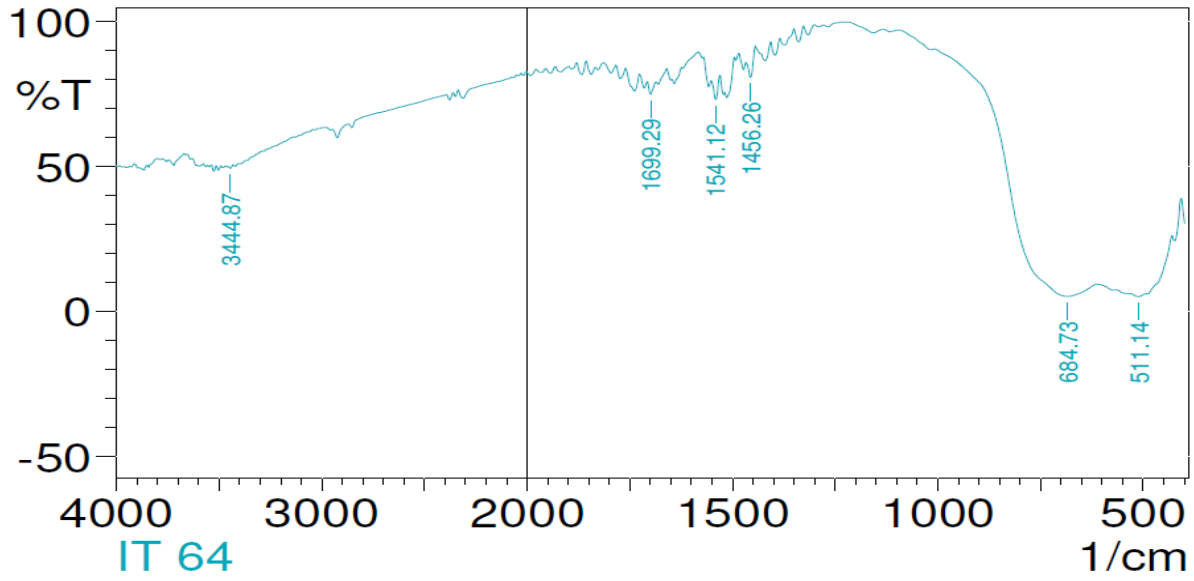

Figure 24: IR spectrum of S,N-TiO_2 (1:4,600^{0}C) photocatalyst

Table 26: IR intensities of 1:4,600^{o}C S,N-TiO_2 photocatalyst

Peak	Intensity	Correction intensity
511.14	5.149	1.049
684.73	5.276	19.212
1456.26	80.804	8.058
1541.12	73.095	7.579
1699.29	74.93	4.394
3444.87	49.47	0.919

3.3 X-Ray Diffraction of the S,N-TiO_2 photocatalysts

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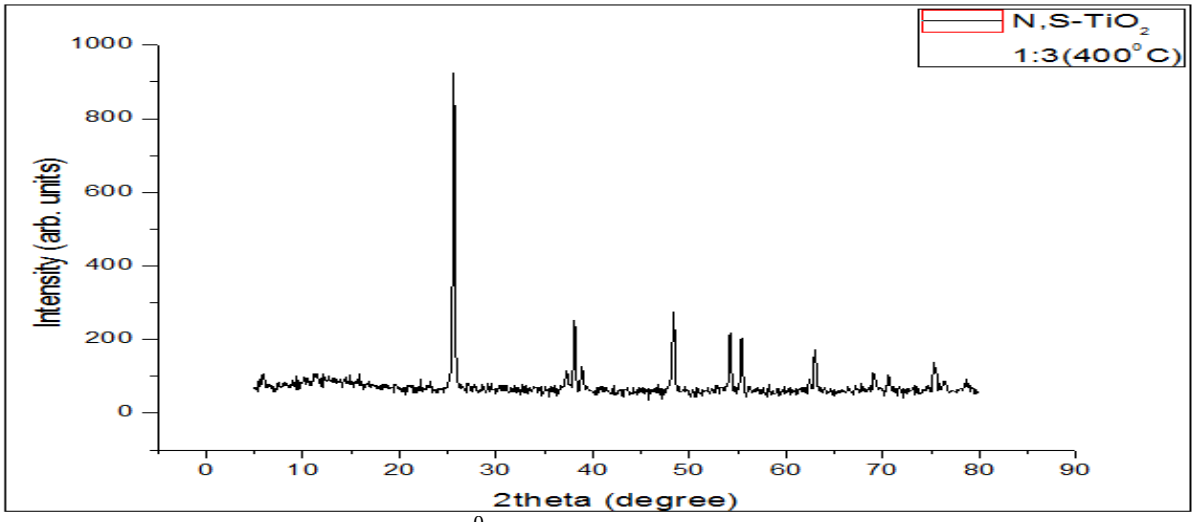

Figure 25: XRD of S,N-TiO_2 (1:3,400^{0}C) photocatalyst

Table 27: XRD intensity of 1:3,400^{o}C S,N-TiO_2 photocatalyst

Strongest Peak	2θ (Degree)	Intensity counts
1	25.6025	404

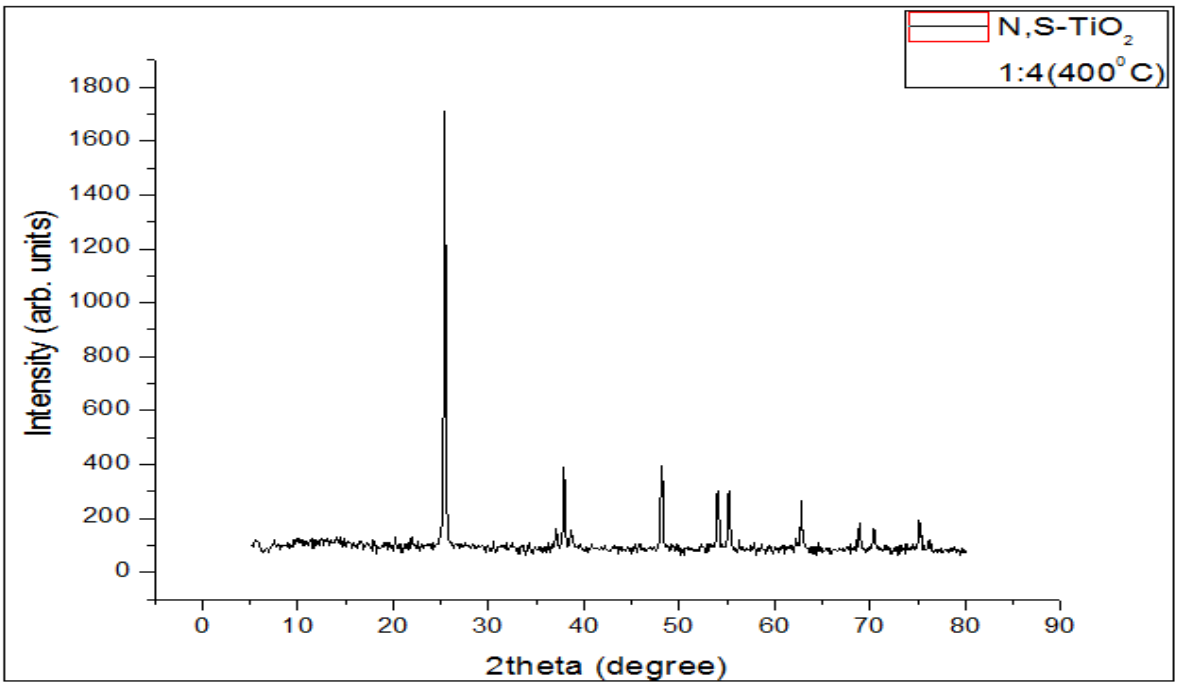

Figure 26: XRD of S,N-TiO_2 (1:4,400^{0}C) photocatalyst

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Table 28: XRD intensity of 1:4,400^{o}C S,N-TiO_2 photocatalyst

Strongest Peak	2θ (Degree)	Intensity counts
1	25.3844	661

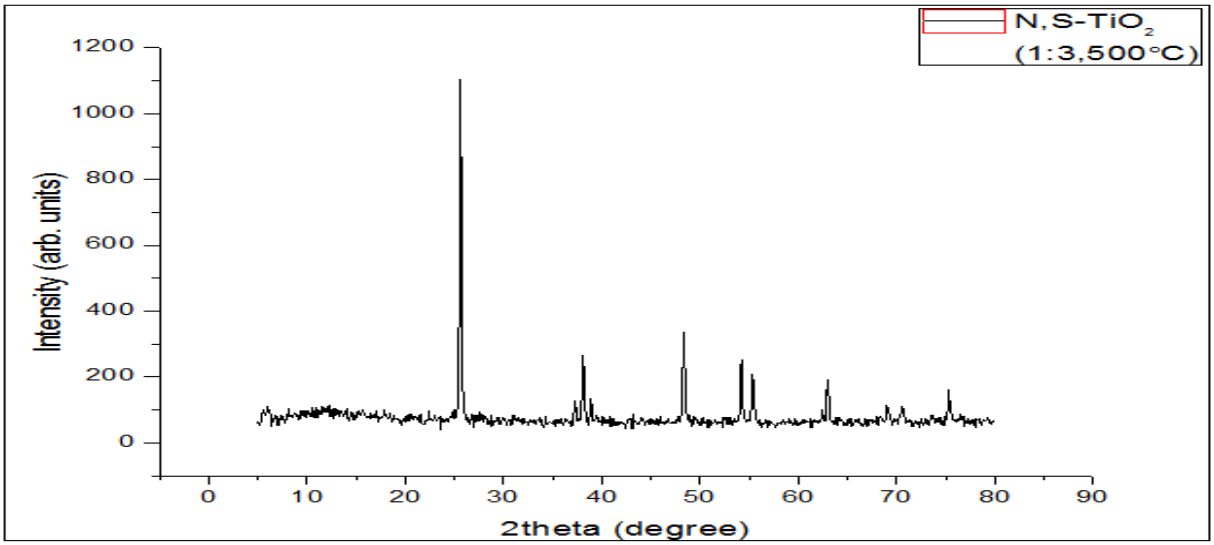

Figure 27: IR spectrum of S,N-TiO_2 (1:3,500^{0}C) photocatalyst

Table 29: XRD intensity of 1:4,400^{o}C S,N-TiO_2 photocatalyst

Strongest Peak	2θ (Degree)	Intensity counts
1	25.5960	448

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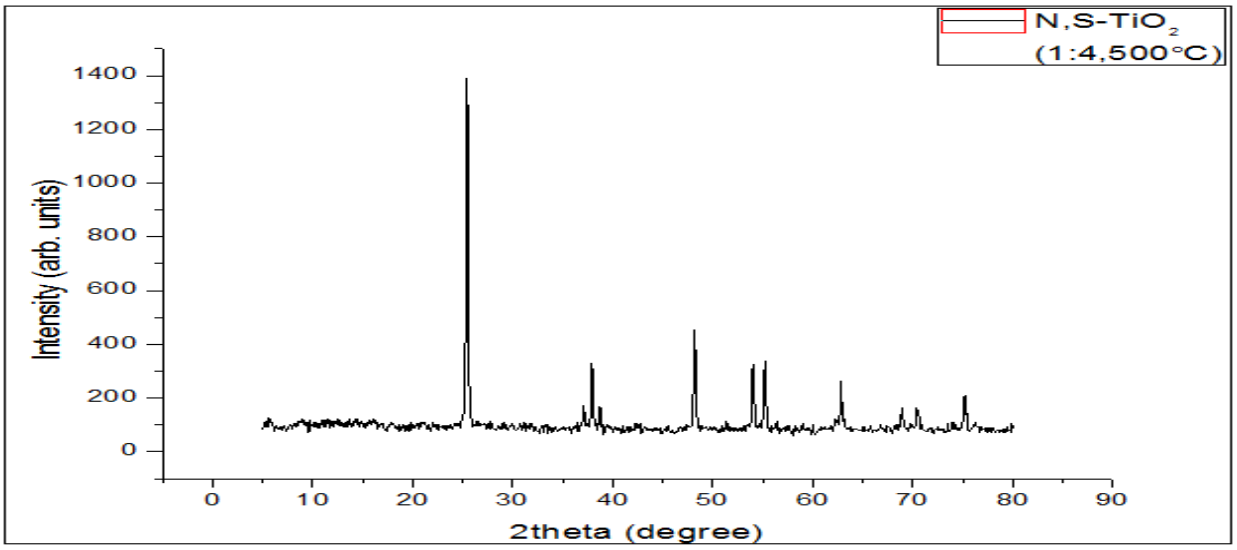

Figure 28: IR spectrum of S,N-TiO_2 (1:4,500^{0}C) photocatalyst

Table 30: XRD intensity of 1:4,500^{o}C S,N-TiO_2 photocatalyst

Strongest Peak	2θ (Degree)	Intensity counts
1	25.4173	608

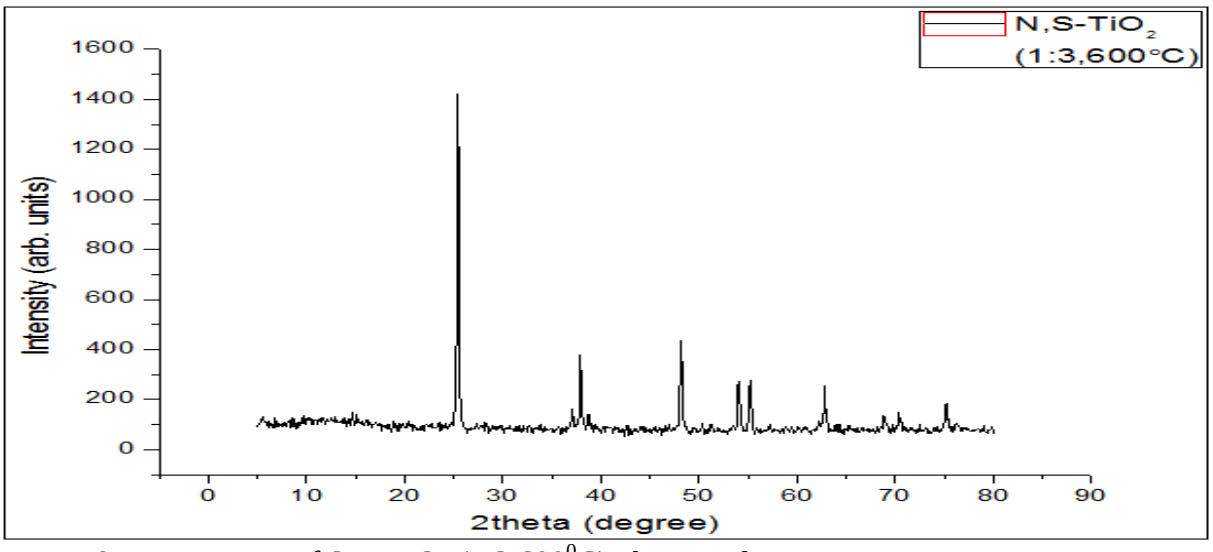

Figure 29: IR spectrum of S,N-TiO_2 (1:3,600^{0}C) photocatalyst

Table 31: XRD intensity of 1:3,600^{o}C S,N-TiO_2 photocatalyst

Strongest Peak	2θ (Degree)	Intensity

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		counts
1	25.4069	599

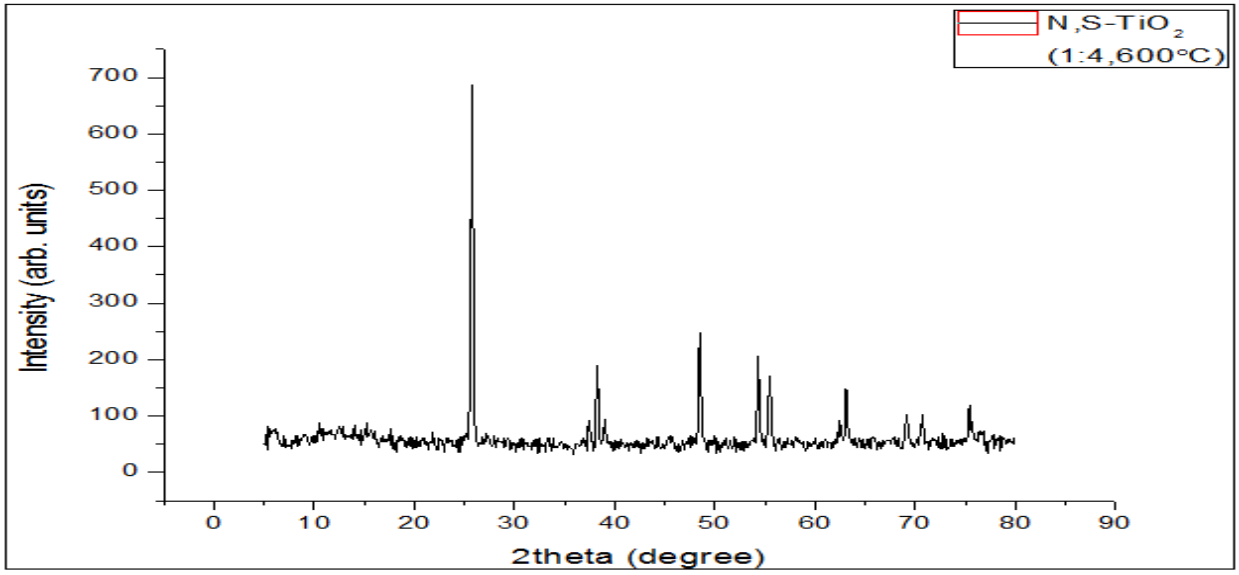

Figure 30: IR spectrum of S,N-TiO_2 (1:4,600^{0}C) photocatalyst

Table 32: XRD intensity of 1:4,600^{o}C S,N-TiO_2 photocatalyst

Strongest Peak	2θ (Degree)	Intensity counts
1	25.7337	296

3.4 Energy dispersive X-Ray analysis of the S,N-TiO_2 photocatalysts

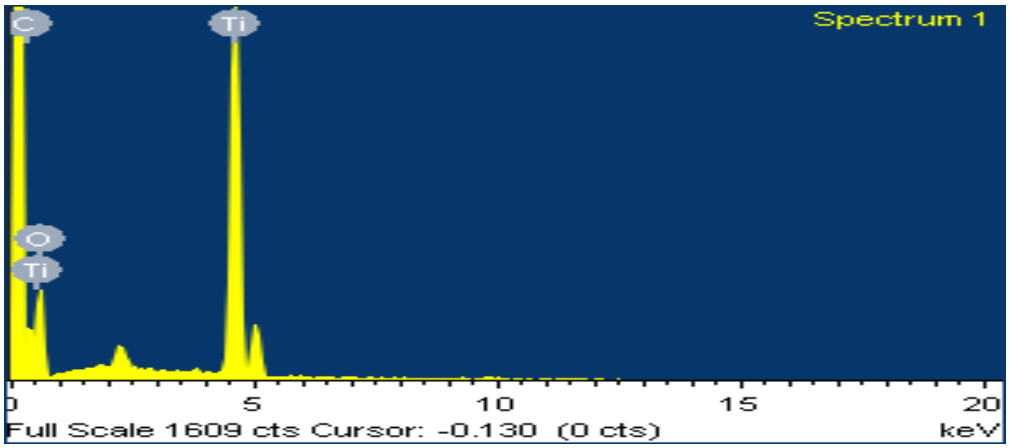

Figure 31: EDAX of 1:3,400^{o}C S,N-TiO_2 photocatalyst

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Table 33: Edax intensities of 1:3,400^{o}C S,N-TiO_2 photocatalyst

Element	Intensity Correlation	Atomic percent
C	0.8336	18.76
O	0.3397	61.71
Ti	0.8845	19.52

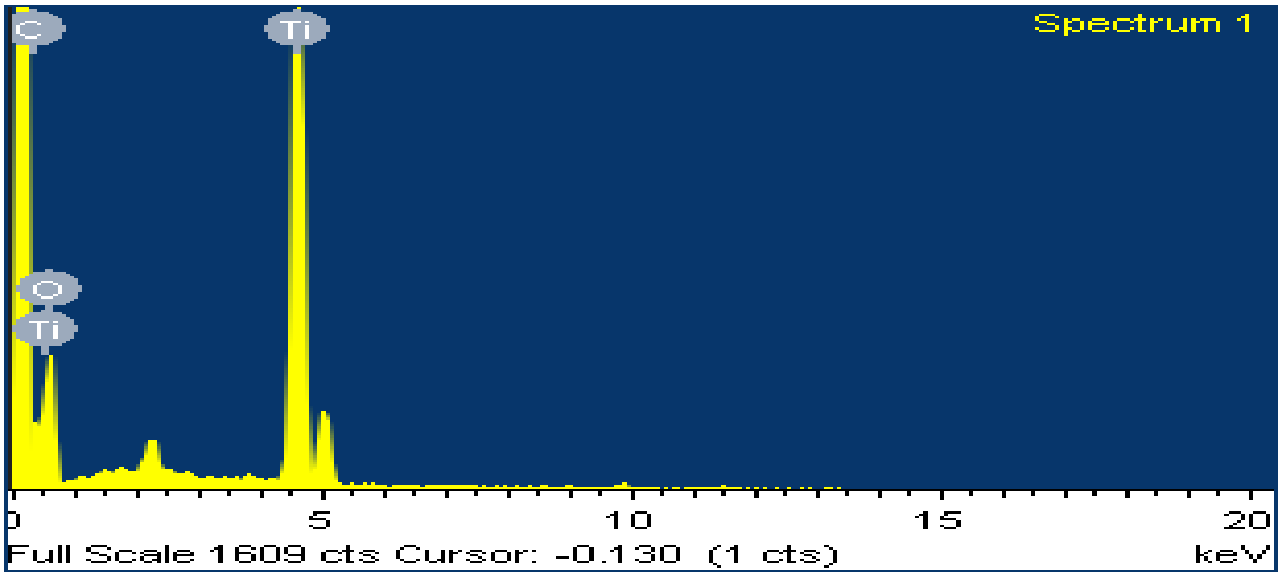

Figure 32: EDAX of 1:4,400^{o}C S,N-TiO_2 photocatalyst

Table 34: Edax intensities of 1:4,400^{o}C S,N-TiO_2 photocatalyst

Element	Intensity Correlation	Atomic percent
C	0.8286	17.36
O	0.3402	62.77
Ti	0.8856	19.88

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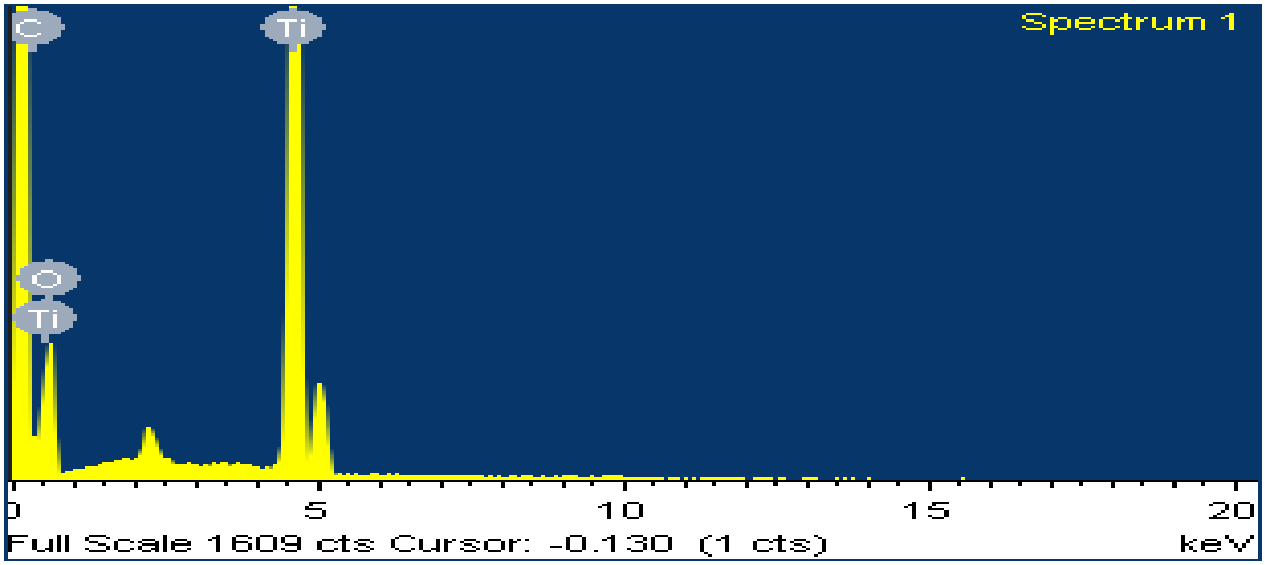

Figure 33: EDAX of 1:3,500°C S,N-TiO_2 photocatalyst

Table 35: Edax intensities of 1:3,500°C S,N-TiO_2 photocatalyst

Element	Intensity Correlation	Atomic percent
C	0.8743	28.40
O	0.3440	55.20
Ti	0.8744	16.30

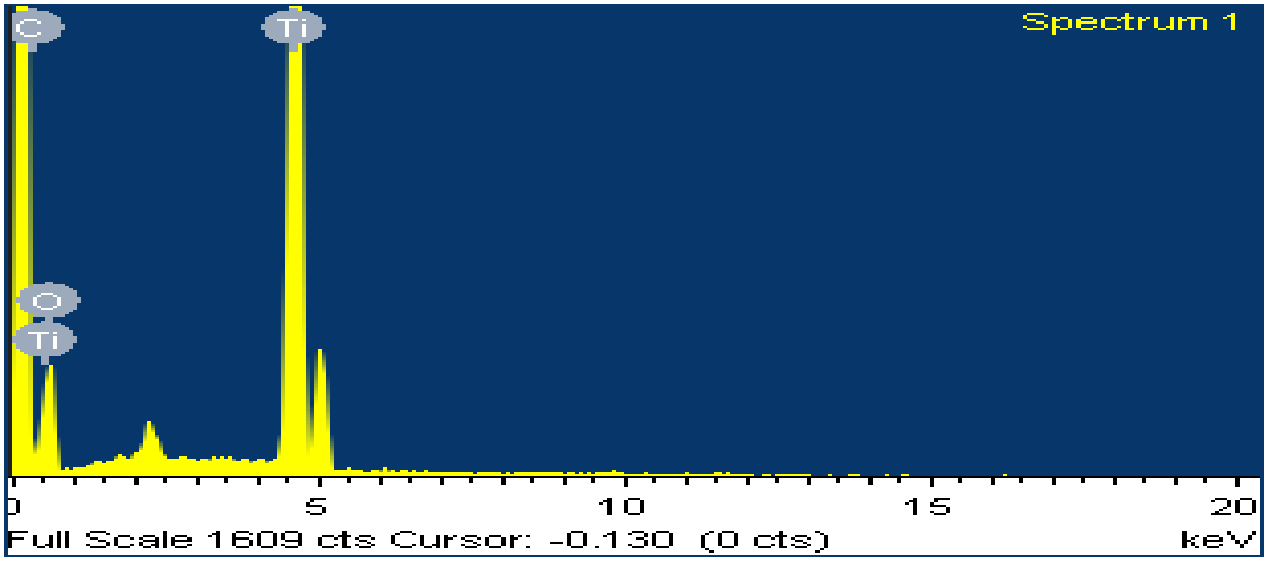

Figure 34: EDAX of 1:4,500°C S,N-TiO_2 photocatalyst

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Table 36: Edax intensities of 1:4,500^{o}C S,N-TiO_2 photocatalyst

Element	Intensity Correlation	Atomic percent
C	0.7802	4.19
O	0.2914	65.09
Ti	0.9128	30.72

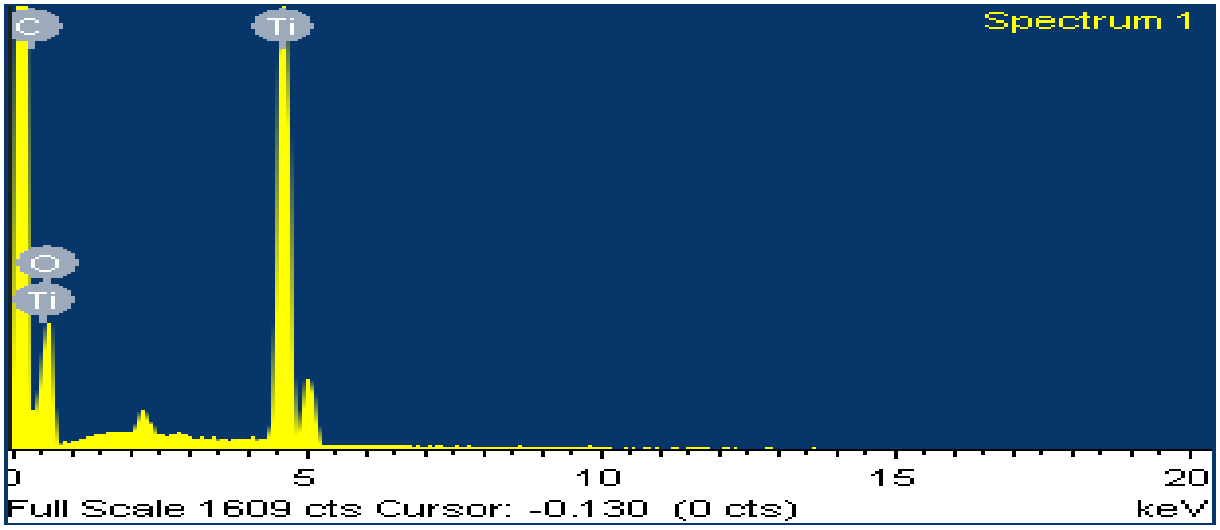

Figure 35: EDAX of 1:3,600^{o}C S,N-TiO_2 photocatalyst

Table 37: Edax intensities of 1:3,600^{o}C S,N-TiO_2 photocatalyst

Element	Intensity Correlation	Atomic percent
C	0.8119	11.77
O	0.3521	67.94
Ti	0.8868	20.29

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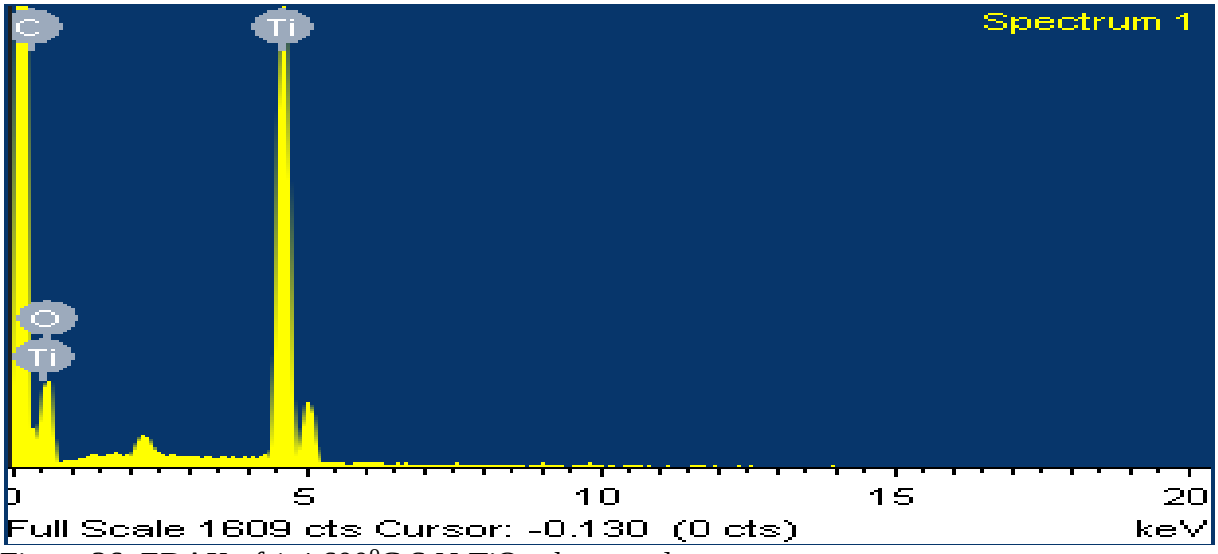

Figure 36: EDAX of 1:4,600°C S,N-TiO_2 photocatalyst

Table 38: Edax intensities of 1:4,600°C S,N-TiO_2 photocatalyst

Element	Intensity Correlation	Atomic percent
C	0.8133	14.01
O	0.3214	62.99
Ti	0.8942	23.00

3.5 Scanning electron microscope images of S,N-TiO_2 photocatalysts

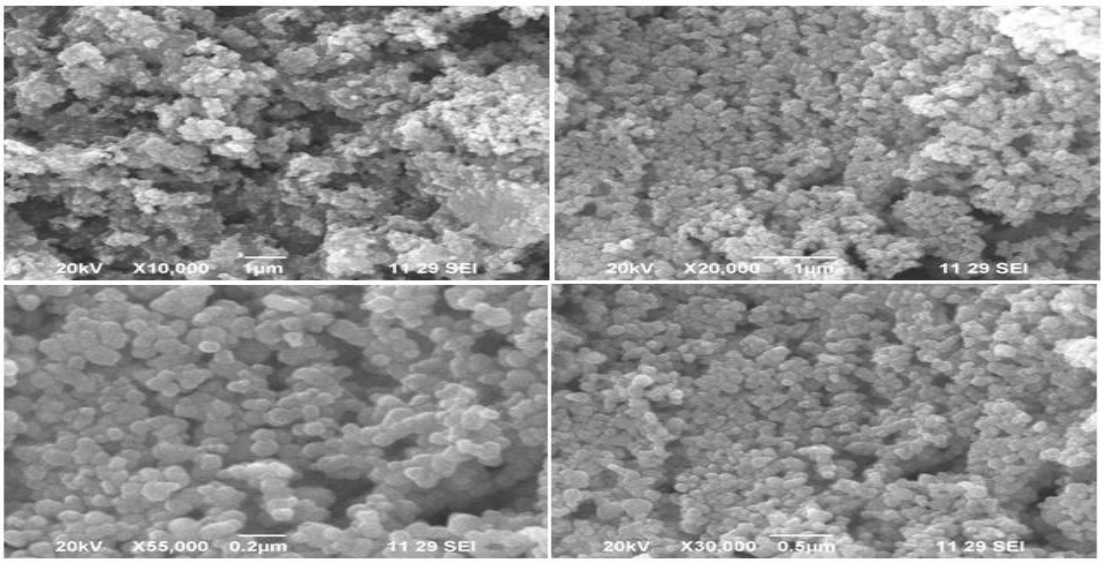

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Figure 37: SEM image of 1:3,400°C S,N-TiO_2 photocatalyst

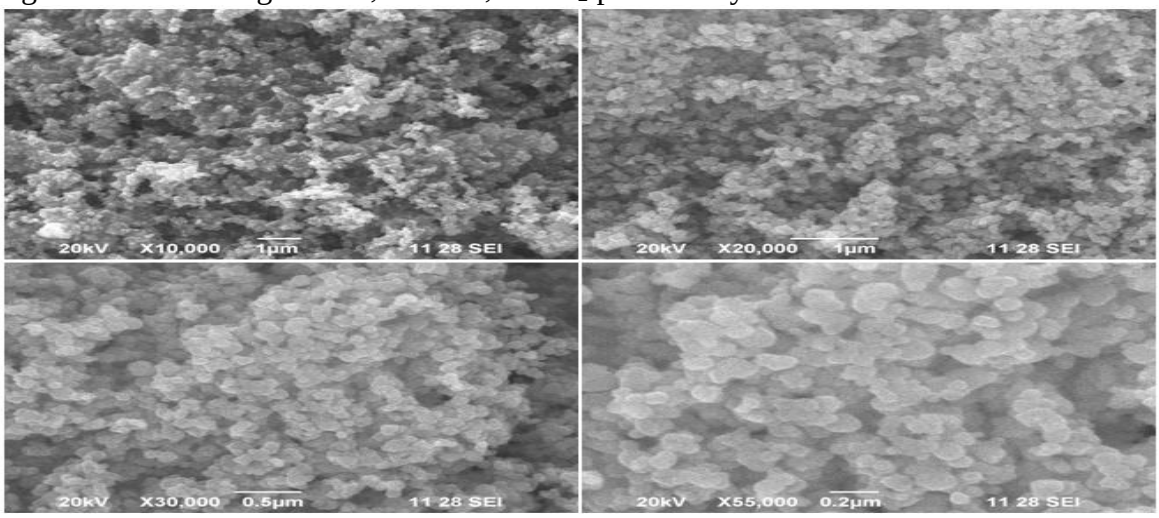

Figure 38: SEM image of 1:4,400°C S,N-TiO_2 photocatalyst

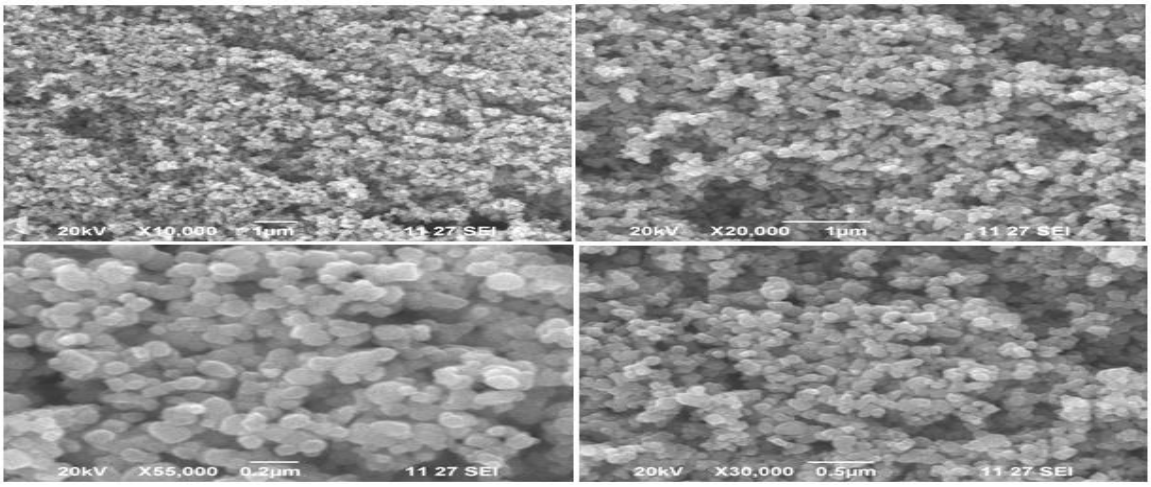

Figure 39: SEM image of 1:3,500°C S,N-TiO_2 photocatalyst

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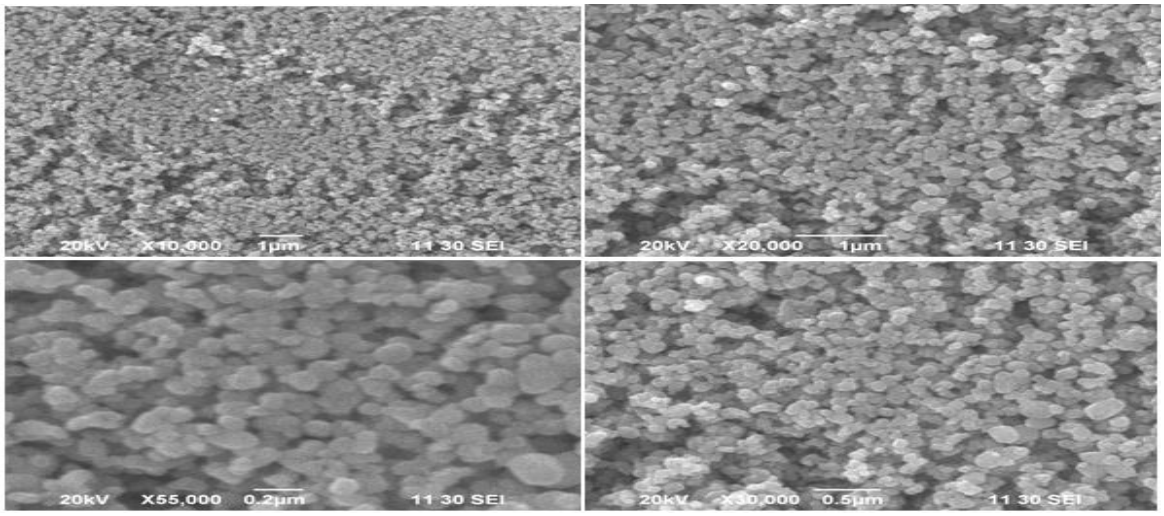

Figure 40: SEM image of 1:4,500^{o}C S,N-TiO_2 photocatalyst

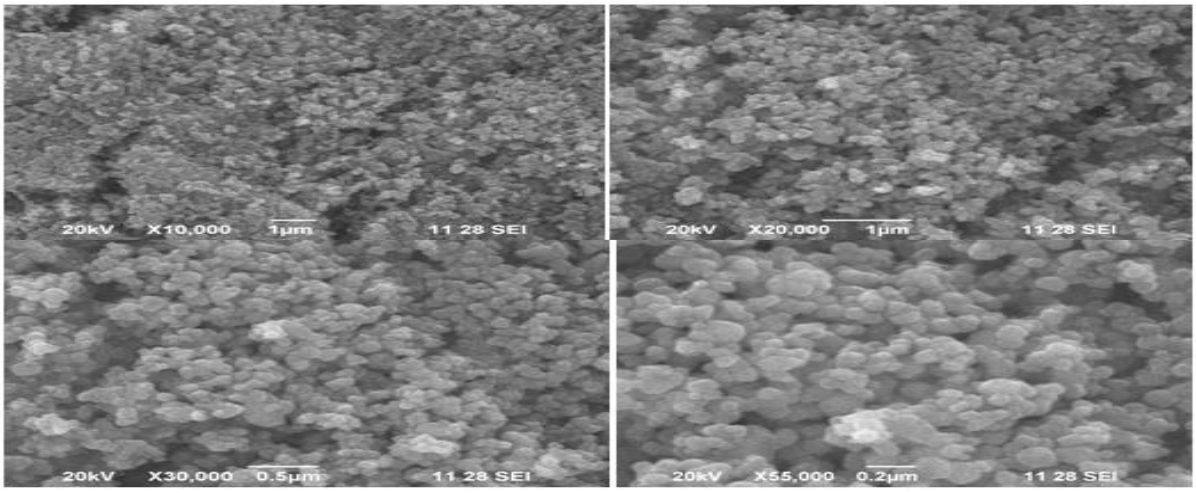

Figure 41: SEM image of 1:3,600^{o}C S,N-TiO_2 photocatalyst

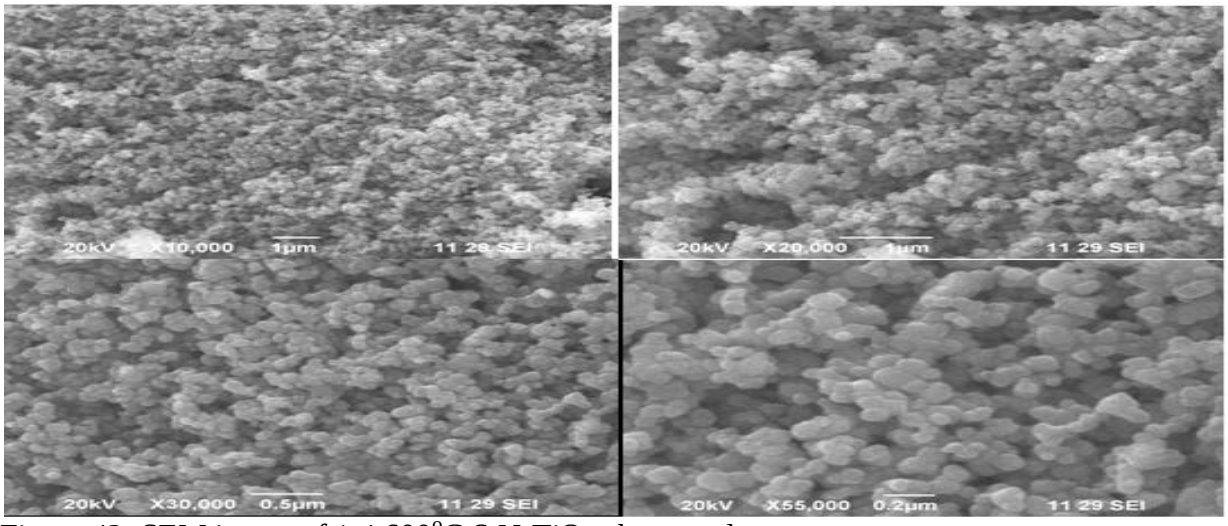

Figure 42: SEM image of 1:4,600^{o}C S,N-TiO_2 photocatalyst

Infrared spectroscopy was taken on a Shimadzu Spectrum RX-I FT-IR Spectrometer in the range of 4000-400 cm^{-1}. Ultraviolet spectroscopy was taken on Systronics 2022 spectrophotometer. SEM, EDAX images were from Joel Ltd , Japan model JSM6390. XRD instrument model 6000 Shimadzu, Japan was used for analysis. The SEM images depict the photocatalyst morphology structure prepared at different temperatures. Atomic percentage and intensity correlation is revealed through the EDAX analysis and XRD patterns. IR spectroscopy shows the band intensities of the photocatalysts revealed in the tabulations.

4. CONCLUSION

An efficient way for the treatment of impure water containing dyes was applied. The absorption of different photocatalysts and the photodegradation effects were specified. Successful synthesis of photocatalysts for studying its activity on the Basic Fuchsine dye was carried out. The structure, photocatalytic activity and optical properties of the sulphur and nitrogen doped titanium dioxide was investigated thoroughly. The samples prepared had enhanced light absorption with band gap decrement in the doped photocatalyst increasing photodegradation. Moreover, interesting discoveries are still needed for modifying compounds and finding its use.

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