

# Structural and Optical Study of TiO<sub>2</sub> Photocatalyst Doped with Thiourea

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## ABSTRACT

The undoped and thiourea doped TiO<sub>2</sub> nanoparticles were prepared via Sol-Gel method by hydrolysis of titanium (IV) isopropoxide with thiourea. The catalyst powder was characterized by powder X-ray diffraction (PXRD), FT-IR and UV-Vis absorption and PL spectral studies. Powder X-ray diffraction analysis show that the structure of the prepared samples are anatase polycrystalline structure. FTIR spectrums for undoped and thiourea doped samples show a broad band between 500 and 800 cm<sup>-1</sup>. The optical study shows that thiourea doping leads to increase in the absorption edge wavelength, and a decrease in the band gap energy of TiO<sub>2</sub> nanoparticles.

**Keywords:** Anatase TiO<sub>2</sub>, Thiourea doping, SEM, Photoluminescence

## I. INTRODUCTION

Because of relatively high activity, chemical stability, low cost, and nontoxicity Titanium dioxide has been widely used as photocatalyst for solar energy conversion, environmental applications such as water and air purification. In order to enhance its application and photocatalytic property, much attention has been made in recent years to modify the TiO<sub>2</sub> with different doping materials. However, it can be activated only by UV light (band gap 3.2 eV). As a result, visible-light driven TiO<sub>2</sub> nanoparticles are highly desired [1]. Doping TiO<sub>2</sub> with nonmetal atoms is an effective way to extend the absorption of TiO<sub>2</sub> from UV to the visible region [2]. In this paper, we have reported the synthesis of undoped and thiourea (CH<sub>4</sub>N<sub>2</sub>S) doped TiO<sub>2</sub> nanopowders by sol-gel method and the structural, morphological and optical characterization results are discussed.

## II. SYNTHESIS OF TiO<sub>2</sub> NANOPARTICLES

TiO<sub>2</sub> nanopowder is prepared via sol-gel method using the precursor Titanium isopropoxide (TTIP, 97%, Sigma Aldrich), deionised water and ethyl alcohol (Merck) as the starting materials. 100 ml of ethyl alcohol is added to 15 ml of TTIP in a beaker. The pH of the above solution is achieved to acidity range using acetic acid. Then the mixed solution is stirred 10

minutes using magnetic stirrer. 10 ml of deionised water is added drop wise to the mixed solution. Now the solution transforms to gel. After aging 24 hours the gel is filtered and dried. Similar to the above reaction suitable amount of thiourea is taken and added drop wise instead of deionised water alone to get the thiourea doped TiO<sub>2</sub> nanopowders. The TiO<sub>2</sub> we get is used for further characterization.

## III. CHARACTERIZATION TECHNIQUES

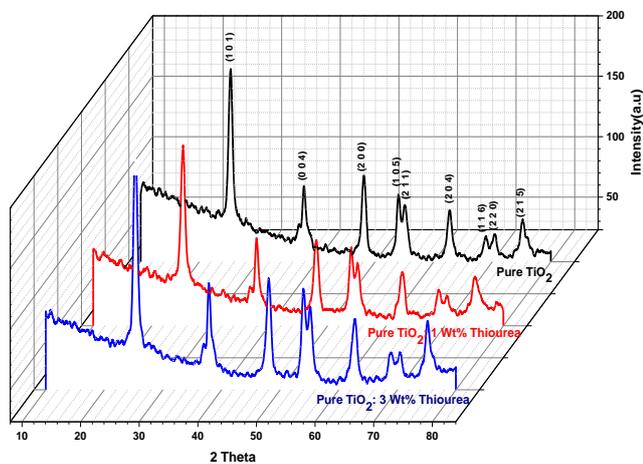
The prepared TiO<sub>2</sub> nanopowder is characterized by Powder XRD using XPERTPRO diffractometer. FTIR spectra of the TiO<sub>2</sub> nanopowders were characterized by Jasco 4100 Spectro Photometer equipped with ATR. UV-Vis absorption spectra of the TiO<sub>2</sub> nanopowders were recorded using SHIMADZU UV-2600 UV-Vis Spectrophotometer. The Photoluminescence spectra of the TiO<sub>2</sub> nanopowders were recorded using Perkin Elmer Fluorescence Spectrophotometer. SEM-EDAX spectra of TiO<sub>2</sub> nanopowders were recorded using JEOL JSM 630LV Scanning Electron Microscope.

## IV. RESULTS AND DISCUSSION

### a) Powder X-Ray Diffraction Analysis

Figure (1) shows the PXRD patterns of undoped TiO<sub>2</sub> and thiourea doped TiO<sub>2</sub> nanoparticles. The diffraction

peaks at  $2\theta = 25.30, 37.83, 48.09, 53.98, 55.17, 62.78, 68.54, 68.91$  and  $75.00$  corresponds to the (101), (004), (200), (105), (211), (204), (116), (220) and (215), respectively for the plane of tetragonal anatase  $\text{TiO}_2$ . The data obtained is agrees with the standard JCPDS file (JCPDS 21-1272).



**Figure 1:** PXRD patterns of undoped and thiourea doped  $\text{TiO}_2$  nanoparticles

Thiourea doped sample shows that similar peaks of anatase structure without any detectable peaks related to dopant ions. This is due to the fact that dopant ions may have been moved either into interstitial positions or substitutional sites of the  $\text{TiO}_2$  nanocrystal structure, or their concentration was too low to be detected [4]. The crystallite size of  $\text{TiO}_2$  nanoparticles was calculated using Debye–Scherrer formula;

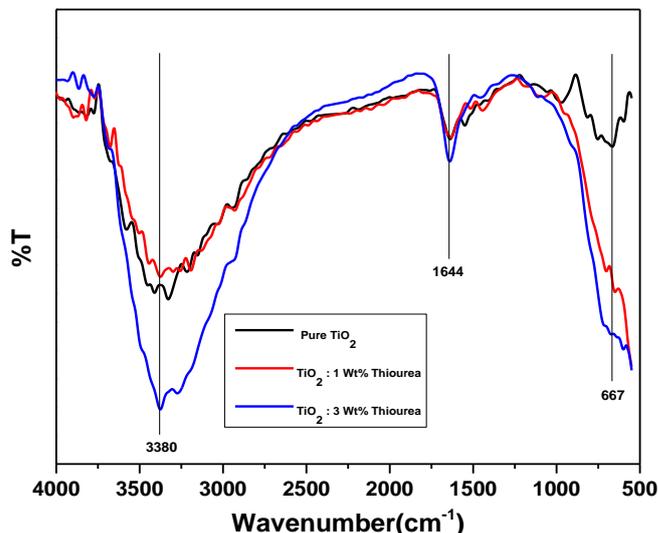
$$D = 0.9\lambda / \beta \cos \theta$$

where  $D$  is the crystallite size,  $\lambda$  is the wavelength of the X-ray radiation ( $\text{CuK}\alpha = 0.154060 \text{ nm}$ ),  $\theta$  is the diffraction angle and  $\beta$  is the full width at half maximum (FWHM) [3]. Using the above formula the crystallite size obtained for undoped  $\text{TiO}_2$  nanoparticles is  $12 \text{ nm}$ . Thiourea doping leads to increase in size of  $\text{TiO}_2$  crystallites.  $18$  and  $23 \text{ nm}$  size particles obtained for  $1$  and  $3 \text{ wt} \%$  thiourea modified  $\text{TiO}_2$  nanoparticles, respectively.

### b) FTIR Spectral Analysis

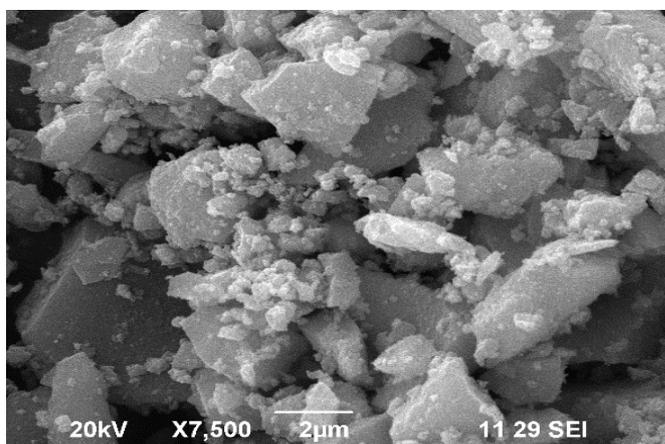
FTIR spectra of the undoped and thiourea doped  $\text{TiO}_2$  nanoparticles are shown in figure (2). The absorption peak at  $3380 \text{ cm}^{-1}$  are assigned to the stretching vibration mode of the O-H group. The absorption peak

at  $1641 \text{ cm}^{-1}$  are assigned to the bending vibration mode of the O-H group. The characteristic vibration of Ti-O stretching vibration peak is observed at  $667 \text{ cm}^{-1}$  [5]. Thiourea doping leads to slight shift in wavenumbers of O-H group and Ti-O characteristic vibrational bonds.

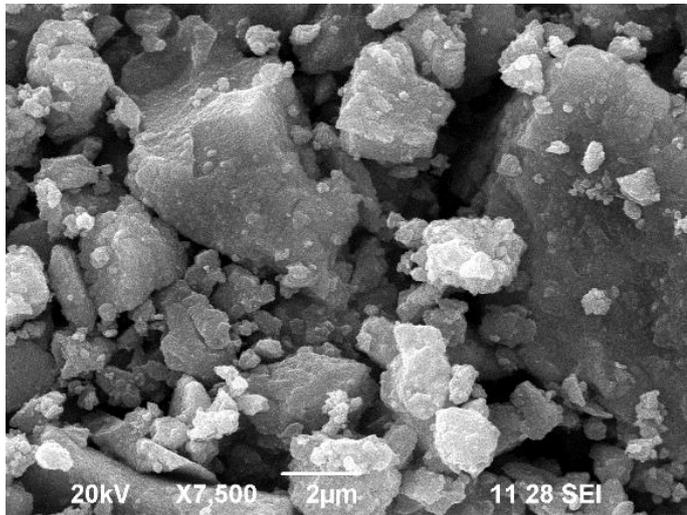


**Figure 2:** FTIR spectra of undoped and Thiourea doped  $\text{TiO}_2$  nanoparticles

### c) SEM Analysis



(a)



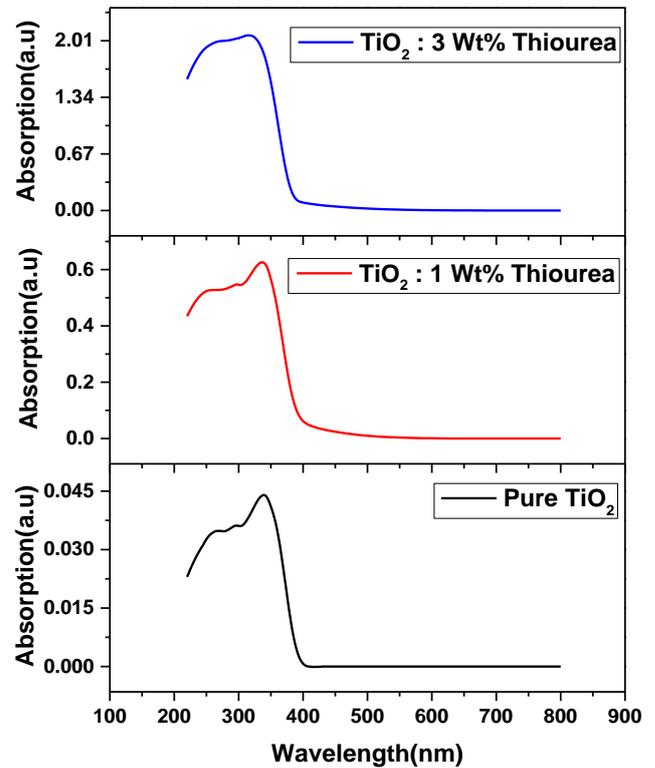
(b)

**Figure 3:** SEM micrograph of (a) undoped and (b) 3 wt% Thiourea doped TiO<sub>2</sub> nanoparticles

SEM images of undoped and thiourea doped TiO<sub>2</sub> agglomerates are presented in figure (3). It is obvious that the particles agglomerated during synthesis and drying. They show morphology like aggregated plates.

#### d) UV-Vis Spectral Analysis

The changes of UV-Vis absorption spectra of undoped and thiourea doped TiO<sub>2</sub> with two different thiourea content are shown in figure (4). The absorption edge shifts to longer wavelength from 382 to 393 nm when doped with thiourea from 1 wt% to 3 wt%. Hence, the bandgap decreases from 3.2 to 3.1 eV. Similar results were previously reported by J.Yuan et al. [6].

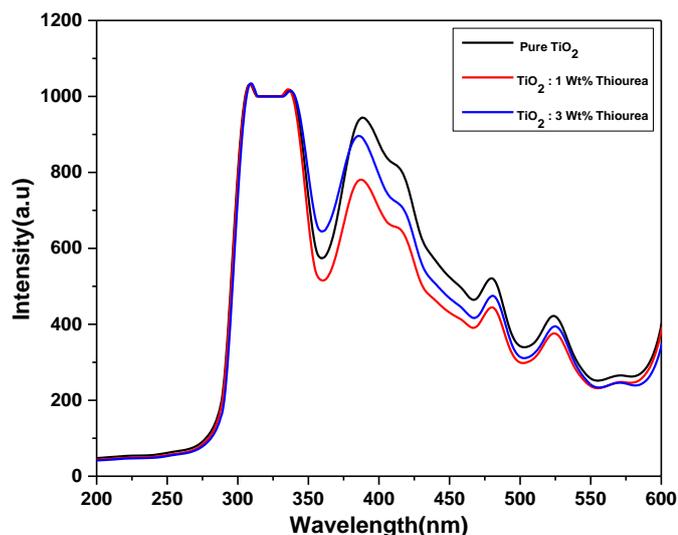


**Figure 4:** UV-Vis absorption spectra of undoped and thiourea doped TiO<sub>2</sub> nanoparticles

#### e) Photoluminescence Spectral Analysis

Self-trapped excitons, oxygen vacancies, and surface states (defects) are the three kinds of physical origins in PL spectra of TiO<sub>2</sub> based materials [7]. PL emission spectra are used to disclose the efficiency of trapping, migration, and transfer of a charge carrier, and the transfer of an electron-hole pairs in semiconductors [5, 8]. Figure (5) shows the PL emission spectra of undoped and thiourea doped TiO<sub>2</sub> nanoparticles. Broad emission in the spectral range from 300 to 550 nm is observed for all the three samples. The emission band at 338 nm in the UV region is associated with the intrinsic emission and is called excitonic emission. The peak at 415 nm is assigned to the blue-violet region and is due to charge recombination in the surface state defects. The bands at 480 nm is assigned to blue region which is due to the oxygen vacancies, titanium vacancies, and interstitial defects in the TiO<sub>2</sub> lattice. A green emission can be seen at 524 nm which is due to transitions from the conduction band to oxygen antisites [7]. It should be noted that the PL intensity decreases for thiourea doped TiO<sub>2</sub> nanoparticles. ie: the crystallinity of TiO<sub>2</sub> nanoparticles decreases for low temperature or without annealing and it cause the raise in the density of the defect states. As a result, the trapping of an electron in the defect states increased in which the non-radiative

transition of photo excited charge carriers were upgraded, thus the depress of luminescence is observed [8].



**Figure 5:** PL emission spectra of undoped and Thiourea doped TiO<sub>2</sub> nanoparticles

## V. SUMMARY AND CONCLUSIONS

Undoped TiO<sub>2</sub>, and thiourea doped of TiO<sub>2</sub> nanopowders are synthesized by hydrolysis of TTIP. The XRD patterns indicate that all the samples are in anatase phase. The morphological study suggests that the undoped and thiourea doped samples agglomerates and form plate like structure. The UV-visible absorption measurement confirms the bandgap of TiO<sub>2</sub> nanoparticles decreases with thiourea doping. The induced photoluminescence is probably due to the consequence of the introduction of oxygen vacancies.

## VI. REFERENCES

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