

Synthesis, Characterization and Photocatalysis of Nanoparticulate N, S-Codoped TiO₂

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ABSTRACT

An efficient, visible light active, N, S-codoped TiO₂ based photocatalyst was prepared using thiourea as single dopant source. Nanocrystalline N,S-codoped TiO₂ powder were synthesised by manual mixing of TiO₂ powder prepared from titanium(IV)isopropoxide and thiourea in agate mortar. The as prepared doped TiO₂ powder were calcined at 600 °C and were characterized by X-ray diffraction (XRD), FTIR and diffuse reflectance spectra (DRS). N, S-codoped TiO₂ catalysts exhibited stronger absorption in the visible light region with a red shift in the adsorption edge. The photocatalytic activities of the catalysts were evaluated by the degradation of methylene blue dye in aqueous solution. These photocatalysts showed higher activity under both UV and solar light irradiation. Highest activity was achieved for the sample of TiO₂ with lower concentration (1:1) of thiourea. This is attributed to the synergetic effects of red shift in the absorption edge, higher surface area and the inhibition of charge carrier recombination process.

KEY WORDS: Photocatalysis, nanoparticulate, dopant.

1. INTRODUCTION

Organic compounds are widely used in industry as well as in daily life and are common pollutants in water bodies. As they are known to be toxic and carcinogenic, an effective and economic treatment for eliminating the organic pollutants in water has been found to be an urgent demand. Heterogeneous photo catalysis, a promising technology in environmental clean-up, is mostly based on the semiconductor photocatalyst. Nano crystalline titanium dioxide (TiO₂) in particular, anatase-type TiO₂ shows high photocatalytic activities and has already found numerous applications in the removal of pollutants from air and water. However, an important drawback of TiO₂ for applications in photocatalysis is that its band gap is in the range of 3.0-3.2 eV. Thus, the overall photocatalytic efficiency of TiO₂ is limited to only a small fraction of the solar spectrum corresponding to the UV region, which accounts for ~4% of the incident solar energy.

In recent years, shifting of the absorption spectrum of TiO₂ from the UV region into the visible region has attracted much attention. Reducing the size of the band gap by introducing energy levels between the conduction band and valence band allows TiO₂ to be active under visible light. This is the basic idea of metal/non-metal doping in TiO₂ to improve the photocatalytic activity from UV light into visible region. Doping can be achieved using metal and non-metal ions through different synthesis methods such as sol-gel process, hydrothermal synthesis, electro-spinning and magnetron sputtering. In the case of non-metal doping of TiO₂, incorporation of dopants (N or S) by different ways such as sol-gel, hydrothermal synthesis and solvothermal process has been used the most frequently. In particular, depending on the preparation method it has been possible to obtain Nor S-doped TiO₂ with interstitial or substitutional N-doping, leading to materials with different photocatalytic activities. Recent studies have shown that the visible light-induced electron promoted to the conduction band might be responsible for the photocatalytic activity on N-TiO₂. By taking TiO₂ precursor and thiourea as the non-metal doping source, it is easy to intercalate thiourea into the inner space of TiO₂. The mixtures were then subjected to calcination at certain temperature to get non-metal doped TiO₂ with nano dimension from the intercalated compound. The as-prepared materials exhibit enhanced photocatalytic activity for degradation of methylene blue under both UV and visible light irradiation. In this study, we report on the preparation, characterization and photocatalytic activity towards methylene blue of N, S-codoped TiO₂ materials. The characterization of these materials was performed using various spectroscopic techniques, including diffuse reflectance spectroscopy, Infrared spectroscopy, Raman spectroscopy and X-ray diffraction studies.

2. EXPERIMENTAL SECTION

2.1. Preparation of Photocatalysts: The reagents used in this study were titanium isopropoxide (Ti(OPr)₄) and thiourea. To synthesise TiO₂, titanium isopropoxide (29.7 mL, 100 mmol) was placed in a 250 mL beaker. To the above solution 180 mL water was added and this was stirred for 2 hr and dried at 80 °C for 24 hrs. The above

prepared TiO₂ was manually mixed with thiourea in a 4:1 ratio. Subsequently, the mixed material was annealed in ceramic crucible. The annealing process was performed for 2 hr at 600 °C under air atmosphere with the heating rate of 5 °C min⁻¹, which was then followed by cooling at room temperature. This allowed for different amounts of gaseous oxygen to reach the catalyst surface. The weight (%) of thiourea was controlled at 0, 1, 4 and 8 % and the samples obtained were labelled as T0, T1, T4 and T8 respectively.

2.2. Characterization: The catalysts were characterized by various techniques like XRD, FTIR, Raman and UV-Vis DRS. The Fourier transform-infrared spectra (FTIR) were recorded on a Jasco FTIR spectrometer using KBr self-supported pellet technique. UV-Vis diffused reflectance spectra (UV-Vis DRS) was from UV-Vis Jasco spectrometer. XRD patterns of the calcined samples were obtained with a Siemens D 500 X-ray diffractometer in the diffraction angle range of 2θ=10–70° using CuKα radiation. The amount of anatase TiO₂ phase present in the sample was calculated from the Spurr equation.

$$F_A = 100 - \left[\frac{1}{1 + 0.8(I_A(101)/I_R(110))} \right] 100$$

Where F_A is the mass fraction of anatase in the sample, I_A(101) and I_R(110) is the integrated main peak intensities of anatase and rutile respectively. The crystal size of the sample was calculated from the Scherrer equation (eq 2).

$$\beta 0.9\lambda T = \beta \cos \theta$$

Where T = crystallite size, λ = X-ray wavelength, θ = Bragg angle, and β = full width at half maxima (fwhm).

2.3. Photocatalytic Experiments: Methylene blue solution having concentration of 10⁻⁴M was freshly prepared by dissolving in deionized water. All the photocatalytic experiments were carried out at same concentration. Prior to light experiments, dark (adsorption) experiments were carried out to eliminate error due to the adsorption effect. For solar and UV light experiments, methylene blue solution of 50 mL was taken in a beaker with 0.1g of the catalyst. To check the photocatalytic activity in UV light, measurements were carried out using a LZC-4X-Luzchem photoreactor with a UV light intensity of 600lux. For solar photocatalysis, experiments were carried out at the Calicut University Campus, Kerala, India (altitude: 11° 7' 34" North 75° 53' 25" East, time 12.00 A.M. to 2.00 P.M., temperature: 26 ± 1 °C) in August and September 2015 in the presence of natural sunlight having varying lux-intensity in between 50,000–70,000. The standard measurement of sunlight intensity was performed using a Lutron, LX-107HA lux meter. The samples were collected at regular intervals during photocatalytic reactions, centrifuged and the degradation rates were calculated from absorption values of MB measured using the UV-VIS Spectroscopy.

3. RESULTS AND DISCUSSION

3.1. Characterization

3.1.1. XRD: To investigate the phase structure of the prepared samples XRD was used and the results are shown in Figure 1. It can be seen that the prepared catalysts (T0 to T4) exhibits only the characteristic peaks of anatase (major peaks at 25.36, 38°, 48°, 53.9°, 55°) and no rutile phase is observed. These results showed that obtained TiO₂ are phase pure and anatase phase is stabilised using this preparation method and is in agreement with earlier studies. By applying Debye-Scherrer equation, calculated the average particle size and are shown in Table 1. As the concentration of thiourea is increased from 1 molar to 8 molar, the crystal size is increase from 12.6 to 17.0 nm.

Table 1 Crystallite size of anatase

Samples	Crystallite size of anatase (nm)
T0	18.1
T1	12.6
T2	14.2
T3	17.0

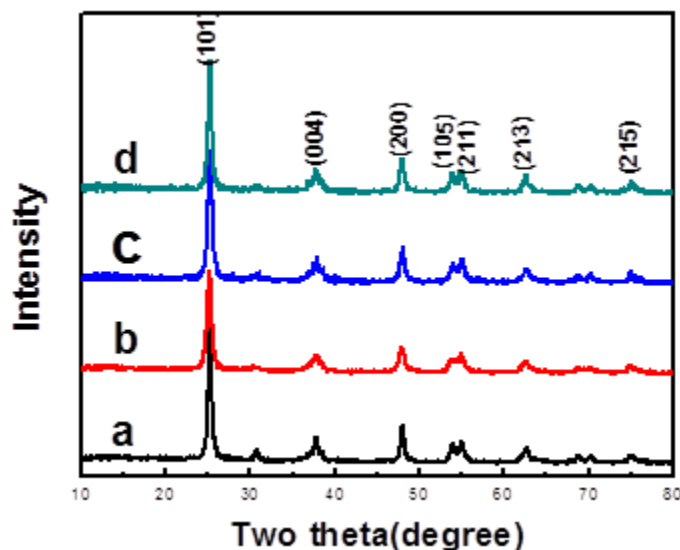


Figure.1.XRD patterns of the catalysts: (a) T0 (b) T1 (c) T2 (d) T3.

3.1.2. FTIR Spectra: Figure 2 shows the FTIR spectra of T0 and T1 catalysts after calcination at 600°C. The absorption bands 3404, 1630 cm^{-1} are assigned to the stretching vibration and bending vibration of the hydroxyl group respectively present on the surface of TiO_2 catalyst. The bands at 1130, 1040 cm^{-1} are corresponding to nitrite and hyponitrite groups present in N,S co-doped TiO_2 sample (T1) and they were absent in undoped TiO_2 sample (T0) which shows successful doping of nitrogen into the lattice of TiO_2 . Absence of peak corresponding to 3189 and 1400 cm^{-1} (Peak of NH_4^+) shows that nitrogen is present only in the form of nitrite and hyponitrite species. Other N,S co-doped sample (T2 and T3) showed similar behavior.

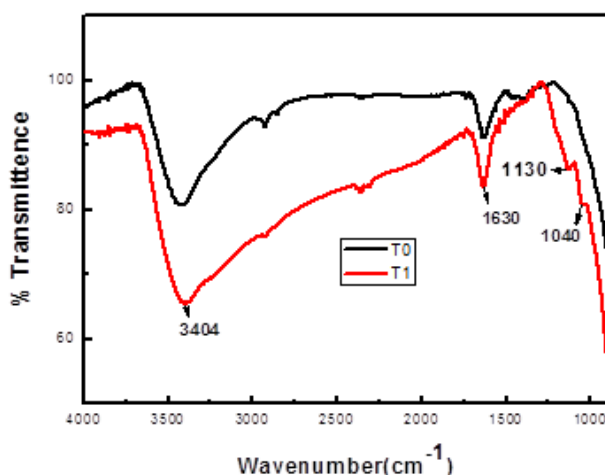


Figure.2.FTIR spectra of T0 & T1 catalysts

3.1.3. Optical Measurements: The UV-Vis diffuse reflectance spectra (DRS) of the catalysts calcined at 600 °C are shown in Figure 3. Band gap energy (E_g value) of all the catalysts is estimated from the plot of absorbance versus photon energy ($h\nu$). The absorbance is extrapolated to get the band gap energy of the catalyst with good approximation as observed in Figure 3. The estimated band gap energies of T0, T1, T4 and T8 are 3.19, 3.04, 3.01 and 2.97 respectively. Furthermore, the red shift in the DRS band increases with the decrease in concentration of thiourea, which is beneficial for improving the photo absorption and ultimately photo catalytic performance of TiO_2 .

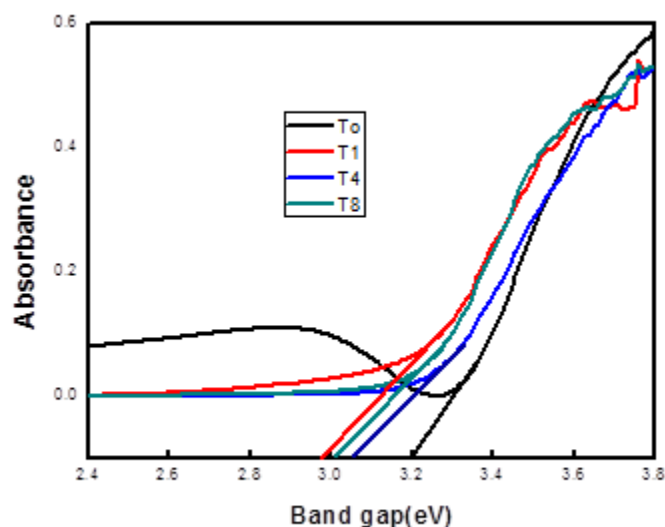


Figure 3. UV-Vis diffusion reflectance spectra of T0, T1, T4 & T8 catalysts

3.2. Photocatalytic Activity: Nanocrystalline TiO_2 exhibits photocatalytic activity in the presence of UV light and it can decompose organic pollutant. The activity depends upon several factors such as the rate of electron-hole recombination, the number of electrons created, the phase composition (anatase or rutile), surface area, crystallinity as well as crystallite size of the TiO_2 and the adsorption properties of the dyes on the surface of the photocatalyst TiO_2 used. The N,S modified sample exhibited higher photocatalytic activity than the control sample T0 prepared under identical conditions.

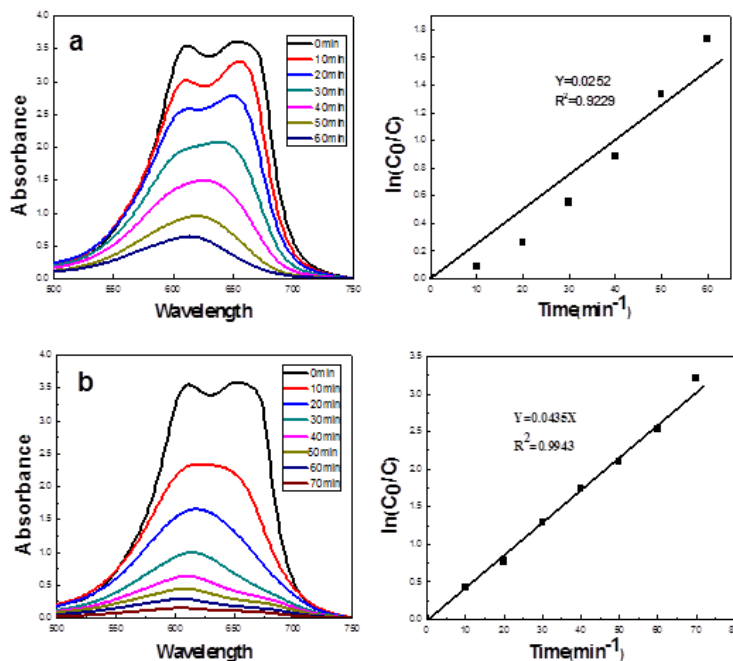


Figure 4. Absorption spectra and kinetic study of methylene blue degradation using (a) the control T0 and (b) T1 samples calcined at 600 °C under UV light. C_0 is the initial absorbance, and C is the absorbance after a time for the methylene blue degradation

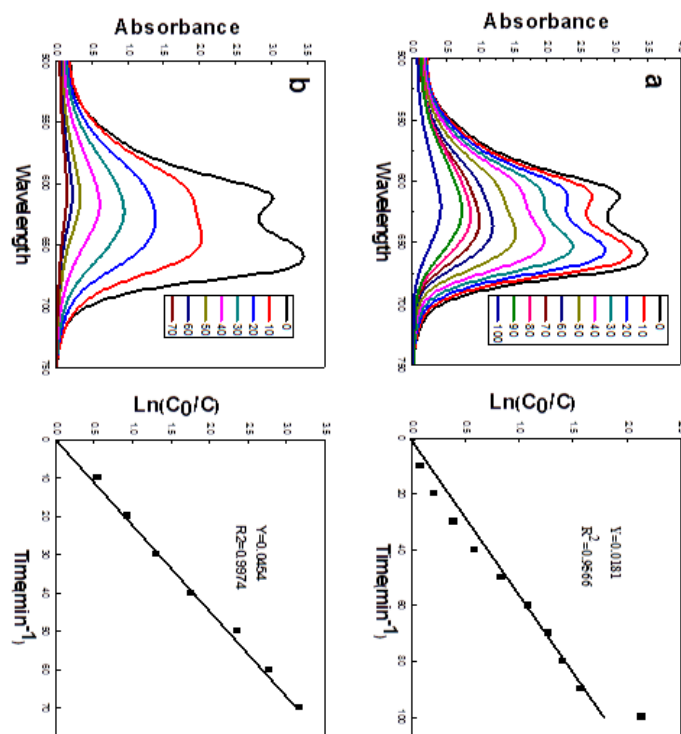


Figure 5. Absorption spectra and kinetic study of methylene blue degradation using (a) the control T0 and (b) T1 samples calcined at 600 °C under sunlight. C_0 is the initial absorbance, and C is the absorbance after a time for the methylene blue degradation

Photocatalytic studies were carried out on T0, T1, T4 and T8 at calcination temperature 600 °C. The details of photocatalytic study with rate constant of the reaction both under UV and sunlight were shown in Table 2. From the Table 2 it is clear that all N, S co-doped TiO_2 sample showed higher activity than the undoped TiO_2 sample. N, S co-doped TiO_2 sample (T1) calcined at 600 °C was found to be the most photocatalytically active (Figure 4(b) and 5(b)) under the visible light irradiation. It completely degraded the methylene blue within 50 min with a rate constant 0.454 min^{-1} whereas the undoped TiO_2 sample showed took more than 100 min with a rate constant of 0.018 min^{-1} .

Table.2. Reaction rate constants (k/min^{-1}) for the degradation of methylene blue using sample calcined at 600 °C.

Sample	UV light	Sunlight
T0	0.0252	0.0181
T1	0.0435	0.0454
T4	0.0325	0.0378
T8	0.0334	0.0391

4. CONCLUSIONS

The present study demonstrates the preparation of N and S co-doped TiO_2 photocatalyst and its role in photocatalytic degradation of methylene blue. The N and S doping can shift the absorption edge of TiO_2 to the visible range and reduce the band gap. The results conclude that 1 wt% thiourea doped TiO_2 (T1) is an efficient catalyst among the various sample prepared for the photocatalytic degradation of methylene blue under visible light. The higher activity of T1 catalyst is collectively due to the anatase phase, stronger adsorption in visible light region along with high surface area and lower electron-hole recombination of anatase phase structure.

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