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 a 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 dyes 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 photocatalysis, 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)₃) 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 TiO$_2$ 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 CuK$\alpha$ radiation. The amount of anatase TiO$_2$ phase present in the sample was calculated from the Spurr equation.

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

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, $\lambda$ = X-ray wavelength, $\theta$ = Bragg angle, and $\beta$ = full width at half maxima (fwhm).

2.3. Photocatalytic Experiments: Methylene blue solution having concentration of 10$^{-4}$M 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 with0.1g 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>
<thead>
<tr>
<th>Samples</th>
<th>Crystallite size of anatase (nm)</th>
</tr>
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<tbody>
<tr>
<td>T0</td>
<td>18.1</td>
</tr>
<tr>
<td>T1</td>
<td>12.6</td>
</tr>
<tr>
<td>T2</td>
<td>14.2</td>
</tr>
<tr>
<td>T3</td>
<td>17.0</td>
</tr>
</tbody>
</table>
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 were showed similar behavior.

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 (hv). 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\(_2\).
3.2. Photocatalytic Activity: Nanocrystalline TiO₂ 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 TiO₂ and the adsorption properties of the dyes on the surface of the photocatalyst TiO₂ used. The N,S modified sample exhibited higher photocatalytic activity than the control sample T0 prepared under identical conditions.

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

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. C₀ 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 cm$^{-1}$ 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.

<table>
<thead>
<tr>
<th>Sample</th>
<th>UV light</th>
<th>Sunlight</th>
</tr>
</thead>
<tbody>
<tr>
<td>T0</td>
<td>0.0252</td>
<td>0.0181</td>
</tr>
<tr>
<td>T1</td>
<td>0.0435</td>
<td>0.0454</td>
</tr>
<tr>
<td>T4</td>
<td>0.0325</td>
<td>0.0378</td>
</tr>
<tr>
<td>T8</td>
<td>0.0334</td>
<td>0.0391</td>
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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.
REFERENCES


