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A Facile Urea-Assisted Thermal Decomposition Process of TiO₂ Nanoparticles and Their Photocatalytic Activity

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Abstract: In the present work, we have reported a facile and large-scale synthesis of TiO₂ nanoparticles (NPs) through urea-assisted thermal decomposition of titanium oxydisulphate. We have successfully synthesized TiO₂ NPs by using this effective route with different weight ratios of titanium oxydisulphate: urea. The structures and properties of TiO₂ NPs were confirmed by scanning electron microscope (SEM), transmission electron microscopy (TEM), thermogravimetric analysis (TGA), fourier transform infrared spectroscopy (FT-IR), ultra violet–visible spectroscopy (UV-vis), and photoluminescence (PL) techniques. XRD demonstrated that TiO₂ NPs holds of anatase crystal phase with crystallizing size 14–19 nm even after heating at 600 °C. TGA, SEM, and TEM images reveal urea's role, which controls the size, morphology, and aggregation of TiO₂ NPs during the thermal decomposition. These TiO₂ NPs were employed for photodegradation of Methyl Orange (MO) in the presence of ultraviolet (UV) radiation. An interesting find was that the TiO₂ NPs exhibited better photocatalytic activity and excellent recycling stability over several photodegradation cycles. Furthermore, the present method has a great perspective to be used as an efficient method for large-scale synthesis of TiO₂ NPs.

Keywords: TiO₂; urea; nanoparticles; combustion; photodegradation

1. Introduction

Over the last few decades, more focus has been given to learning the revival of the environment by the degradation of organic and inorganic pollutants to safe or less hazardous molecules. This comprises a sequence of reactions such as redox reactions, metals deposition and detoxification of water [1–3]. Recently, semiconductor metal oxide-based photocatalysis has been given great consideration as a green and efficient technology for the UV irradiation mediated photodegradation of hazardous organic pollutants [4].

In the literature, numerous metal oxides like TiO₂, ZnO, Bi₂O₃ and Fe₂O₃ have been used for the removal of organic water pollutants [5–7]. Among these metal oxides, TiO₂

has emerged as excellent photocatalytic material due to its high optical sensitivity, stability, low cost, non-toxic nature, wide energy bandgap (3.2 eV) and high photocatalytic activity [8]. The TiO₂ NPs have attracted considerable attention because of their unique properties and have attained immense significance in many technological applications, including photocatalysis, solar cells, sensors and memory devices [9].

TiO₂ NPs are synthesized using various methods, including hydrothermal, sol-gel, solvothermal, precipitation, microwave, chemical vapor deposition, etc. [10] However, these methods suffer from drawbacks such as the use of toxic substrates, high-cost equipment, high temperature, complicated procedures and low yields. Compared to these synthetic methods, the thermal decomposition method is a relatively fast, simple, cost-effective and environmentally friendly path for large-scale synthesis of TiO₂ NPs.

As far as a literature survey is concerned, few reports on the synthesis of TiO₂ NPs through thermal decomposition of titanium oxysulphate by using urea without any tedious procedure. This technique has many crucial advantages like using solid, inexpensive, non-toxic precursors (titanium oxysulphate and urea) and can be the first most effortless effort to synthesize TiO₂ NPs. Urea is a widespread and affordable additive widely produced in the agricultural industries. However, additives like urea can influence and control the growth of TiO₂ crystals. Under thermal process, it transforms into graphitic carbon nitride (g-C₃N₄) followed by cyanuric acid with the evolution of gas [11–13]. Thus, urea can be used as a growth controller of the solid-state synthesis of TiO₂ NPs from titanium oxysulphate. The photocatalytic activities and structural, morphological and optical properties of the as-synthesized TiO₂ NPs were studied through various characterization techniques. The catalytic activity of TiO₂ NPs was investigated regarding the degradation of MO under UV irradiation. To attain optimum conditions for photodegradation of methyl orange (MO), the result of different factors such as precursor ratio, temperature, pH of MO solution and catalyst loading has been investigated systematically. Our finding suggests that the thermal decomposition synthesis method has many advantages like being a single step, not using expensive or harsh chemicals and low cost and can be the simplest attempt to synthesize TiO₂ NPs photocatalyst for environmental remediation.

2. Experimental

2.1. Materials

Titanium oxysulphate (TiOSO₄·H₂O, CAS-13825-74-6), urea (CON₂H₄, CAS-57-13-6) and P25 TiO₂ (CAS-13463-67-7) were supplied from Sigma-Aldrich (Bangalore, India), Methyl Orange (CAS-872-50-4) purchased from Molychem (Mumbai, India). All other chemicals and reagents were of analytical grade.

2.2. Preparation of TiO₂ NPs

The TiO₂ NPs have been synthesized by grinding titanium oxysulphate and urea in a mortar and pestle for 15 min; the obtained powder was heated at 600 °C with a heating rate of 15 °C per min in the muffle furnace for 3 h. Subsequently, the product was washed with distilled water, dried in the oven at 80 °C and finally rounded to a fine powder. The pure TiO₂ NPs were synthesized without the addition of urea, and the obtained sample was designated as TU0. The precursors (titanium oxysulphate and urea) with weight ratios of 1:0.100, 1:0.200, 1:0.300, 1:0.400 and 1:0.500 are designated as TU1, TU2, TU3, TU4 and TU5, respectively. The as-synthesized TiO₂ NPs were used for further characterization.

2.3. Characterization

The crystalline phase of TiO₂ was studied by using XRD (Pan analytical Diffractometer, Ultima IV, Rigaku Corporation, Tokyo, Japan) with CuKα radiation (λ = 1.5406 Å). The investigation range of 2θ was 5° to 80°. Thermogravimetric analysis (TGA) was carried out in air at a heating rate of 10 °C per minute on an SDT Q600 (V20.9 Build 20, Mettler-Toledo, Greifensee, Switzerland) instrument. The morphological features of the samples were studied using a scanning electron microscope (SEM) and transmission electron microscopy

(JEM-2010, JEOL, Tokyo, Japan). The FT-IR spectral analyses of samples were carried out on a Bruker Spectrometer in the frequency range, 4000 to 400 cm^{-1} . To analyze the absorption of light by the photocatalysts, UV–Vis diffuse reflectance spectra (DRS) were scanned using UV–Vis spectrophotometer (LAB INDIA Analytical UV-3092, Mumbai, India). Photoluminescence (PL) spectra of the samples were confirmed on a spectrofluorometer (JASCO, Model FP.750, Tokyo, Japan).

2.4. Evaluation of Photocatalytic Performance

Photocatalysis by as-prepared TU0, TU1, TU2, TU3, TU4 and TU5 were assessed for MO as exemplary pollutant at room temperature. In this experiment, 0.1 gm of the catalyst was dispersed in the aqueous dye solution (100 mL, MO = 20 ppm). The photocatalytic activities of the synthesized photocatalysts were examined at ambient temperature under UV light irradiation (HPL-N, 250 W, Philips, Gurgaon, India). Before irradiation, the suspensions were stirred for 30 min in the dark and allowed to obtain the equilibrium adsorption of dye molecules on the surface of the photocatalyst. At given time intervals, 3 mL of aliquot was withdrawn and filtered to remove the photocatalyst. The equilibrium concentration of dye solution was then checked quantitatively using UV-Vis spectrophotometer (Model-UV-3600, Shimadzu, Tokyo, Japan) by measuring the absorbance of MO at 464 nm, throughout the photodegradation process. After each run, the photocatalyst was collected, washed with distilled water and dispersed into fresh MO solution for the next cycle, the absorbance of MO at 464 nm was measured, and the recyclability and stability of the photocatalyst were checked.

3. Results and Discussion

3.1. XRD Analysis

The crystal structure, phase characteristics and purity of TiO_2 were identified using XRD patterns. Figure 1 exhibits XRD patterns of TU0, TU1, TU2, TU3, TU4 and TU5. From Figure 1, the characteristic peaks observed at $2\theta = 25.3^\circ, 37.8^\circ, 48.0^\circ, 53.9^\circ, 55.1^\circ, 62.7^\circ, 68.9^\circ, 70.3^\circ$ and 75.1° , are attributed to (101), (004), (200), (105), (211), (204), (116), (220) and (215), respectively and can be indexed to the crystal planes of tetragonal anatase TiO_2 well matches with JCPDS (Card No. 21-1272) [14]. Anatase phase was confirmed as the first two XRD peaks are well separated ($2\theta = 25.28^\circ$ for d_{101} of anatase versus $2\theta = 27.44^\circ$ for d_{110} of rutile). In addition, the XRD peaks at $2\theta = 30.81^\circ$ correspond to where the d_{121} of the brookite phase is absent, whereas the peak at $2\theta = 62.57^\circ$ confirms d_{204} of the anatase phase [15].

No alteration of peak position and no diffraction peaks from other impurities reveals that the XRD patterns of TU0, TU1, TU2, TU3, TU4 and TU5 contain only the TiO_2 phase and complete combustion of urea. The anatase phase of TiO_2 transforms into a rutile phase at about 600 $^\circ\text{C}$ [16]. On the other hand, XRD patterns of TiO_2 suggest that the anatase phase remains stable even at 600 $^\circ\text{C}$ temperature. Thus, the thermal decomposition is an efficient method for the TiO_2 NPs synthesis from titanium oxysulphate. [17].

From Figure 1, it can also be observed that the (101) direction is the most preferred orientation, and this direction is enhanced as the precursors (titanium oxysulphate and urea) weight ratio increased up to TU4 and slightly decreased thereafter. There are more crystallite planes that are maintained regardless of the increase in precursors (titanium oxysulphate and urea) weight ratio, which indicates the polycrystallinity of the samples.

The lattice parameters for TiO_2 NPs were calculated using the following relation (JCPDS (Card No. 21-1272)):

$$\frac{1}{d_{hkl}^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2} \quad (1)$$

where h, k, l are Miller indices; d is interplanar spacing; a and c are the lattice parameters. The average lattice parameters are found in the range $a = b = 3.804 \text{ \AA}$ and $c = 9.538 \text{ \AA}$, respectively. These are in conformity with standard JCPDS data card values ($a = b = 3.7845 \text{ \AA}$, $c = 9.5143 \text{ \AA}$). Table S1 Supporting information shows the calculated values of lattice parameters.

Figure 1. RD patterns of TU0, TU1, TU2, TU3, TU4 and TU5.

The crystallite size (D) of all the TiO_2 NPs was calculated using Scherer's Equation. [18]

$$D = \frac{0.9\lambda}{\beta \cos \theta} \quad (2)$$

where λ is the wavelength of X-ray employed, θ is the angle of diffraction for the most intense diffraction peak and β is the full width at half maximum of the most intense diffraction peak (FWHM). The diffraction peak (101) was used to calculate the crystallite size of samples. Crystallite sizes of samples are mentioned in Table S1. The crystallite size of TU0, TU1, TU2, TU3, TU4 and TU5 samples are about 19, 18, 17, 16, 14 and 15 nm, respectively. The crystallite size was found to decrease with an increase in urea content up to TU4 and increased slightly thereafter. Table S1 shows the Bragg's angle, interplanar spacing, Miller indices, crystallite size and lattice parameters of TiO_2 NPs synthesized through a facile and large-scale urea-assisted thermal decomposition process.

3.2. TGA Analysis

To understand the thermal decomposition of titanium oxysulphate (TiOSO_4) with urea and thermal stability of TiO_2 NPs, TGA was carried out under air atmosphere from room temperature to 886 °C at a heating rate of 20 °C per minute (Figure 2). For TU4, slight weight loss, observed from 100 to 400 °C, can be ascribed to the slow dehydration of physically adsorbed and intercalated water molecules from $\text{TiOSO}_4 \cdot \text{H}_2\text{O}$ that leads to the formation of TiOSO_4 . However, significant weight loss from 400 to 600 °C can be attributed to the dissociation of SO_3 [19]. Meanwhile, over the entire temperature range, urea is condensed into $\text{g-C}_3\text{N}_4$ through the formation of cyanuric acid at 175 °C, with the evolution of ammonia [20]. However, when the temperature was greater than 550 °C, rapid decomposition and oxidation of $\text{g-C}_3\text{N}_4$ were completed, and the weight loss was found to be 67.9 wt.%.

3.3. SEM and TEM Analysis

The surface morphological features of the TiO_2 NPs synthesized through a facile and large-scale urea-assisted thermal decomposition process are studied by using scanning electron microscopy and transmission electron microscopy. Figure 3 shows the SEM of

TiO₂ NPs synthesized with different urea contents. Figure 3a shows the SEM image of the as-obtained TiO₂ (TU0) without the addition of urea. It is demonstrated that as-obtained TiO₂ particles are found in the form of aggregated and cluster particles.

Figure 2. TGA curve of TU4.

Figure 3. SEM images of (a) TU0, (b) TU1, (c) TU2, (d) TU3, (e) TU4, (f) TU5.

Figure 3b–f shows the SEM image of samples (TU1, TU2, TU3, TU4 and TU5) synthesized by using urea. It is clearly seen that as the concentration of urea increased, a spherical, slightly hierarchical, highly porous, two-dimensional interconnected TiO₂ nanostructure with fine grain sizes was synthesized. Figure 4 shows the low-magnification TEM images of TU4; it can be seen that the TU4 is made up of highly porous and interconnected spherical shaped NPs, which lead to the higher surface area that promotes the photocatalytic performance. [21]. The diameters of the TiO₂ NPs are within the range of 20 to 40 nm, which are prominently consistent with the SEM results. This result shows that urea plays a significant role in the formation and size control of TiO₂ NPs.

Figure 4. TEM images of (a–d) TU4.

To comprehend the phenomenon of alteration in the structure of TiO_2 NPs, we studied the role of urea, temperature and growth rate. TEM images of the TU0 sample exhibit a cluster of TiO_2 . During the synthesis of TiO_2 NPs (TU4), the addition of urea to the titanium oxysulphate precursor caused a reduction in TiO_2 crystal growth. According to preceding reports, urea accelerates the hydrolysis of titanium oxysulphate and converts into cyanuric acid with the liberation of ammonia at $\sim 175^\circ\text{C}$ [19,22]. Consequently, cyanuric acid preferentially adsorbs on the surface of the growth unit and block contact between units; thus, decreases in the length of TiO_2 NPs were observed.

3.4. Optical Properties

Figure 5 presents the UV–Vis diffuse reflectance spectra of TiO_2 NPs. Maximum absorption at 400 nm and a corresponding band gap of 3.10 eV for the TiO_2 NPs suggested that electron hole-pairs can be generated, although the TiO_2 NPs are irradiated with low energy visible light. This also reveals that the optical band gap of the TiO_2 NPs decreased considerably compared to its theoretical value of 3.20 eV [23]. The decrease of band gap can be attributed to different surface state defects [24,25]. The decrease in band gap is due to oxygen vacancies, which led to unique properties for photocatalytic applications [26]. The reduction in band gap is directly proportional to the photocatalytic activity, and TiO_2 NPs show greater activity in the visible region.

3.5. PL Spectra

The separation of the photo-induced electron-hole pair in the TiO_2 NPs was studied by PL emission spectra of TU0, TU1, TU2, TU3, TU4 and TU5. The PL spectra in the 350 to 600 nm wavelength range show excitation at 295 nm as depicted in Figure 6. It was observed that the TU0 exhibited a strong emission band at 470 and 410 nm, which revealed a fast recombination rate of the photoinduced electron-hole pairs. However, the urea used as a precursor during the synthesis of TiO_2 NPs (TU1, TU2, TU3, TU4 and TU5) exhibited a lower PL intensity. Furthermore, the PL spectra indicated that with the increase in urea content, TU4 sample displayed lower PL intensity than TU0, TU1, TU2, TU3 and TU5. This lower PL intensity was ascribed to the presence of oxygen vacancies and defects in TiO_2 NPs, which led to enhancement in their optical properties. Defects and oxygen

vacancies bind the photo-induced electrons easily, which led to giving excitons so that the PL signal can arise easily [26]. The proficient charge separation can enhance the lifetime of charge carriers and boost the efficiency of interfacial charge transfer towards adsorbed dyes. Therefore, the TU4 composite is the superlative sample that displays excellent photocatalysis toward dye degradation.

Figure 5. UV-Vis diffuse reflectance spectra of TU0, TU1, TU2, TU3, TU4 and TU5.

Figure 6. Photoluminescence (PL) spectra of TU0, TU1, TU2, TU3, TU4 and TU5 ($\lambda_{\text{exc.}}$ = excitation wavelength).

3.6. Photocatalytic Degradation of Methyl Orange Using UV Light

The photocatalytic activities of as-synthesized TU0, TU1, TU2, TU3, TU4 and TU5 were individually investigated for degradation of MO as the model pollutant under UV

light irradiation. The concentrations of aqueous MO dye solution were determined from maximum absorbance ($\lambda_{\max} = 464 \text{ nm}$) measurements using UV-vis spectra. The percentage degradation ($D\%$) of MO dye under UV light irradiation over TiO_2 NPs was calculated using a mathematical relation as follows:

$$D\% = \frac{(C_0 - C)}{C_0} \times 100\% \quad (4)$$

where C_0 and C represent initial concentration and final concentration (C), respectively.

The photocatalytic efficiency mostly depends on crystallinity, adsorption ability, surface area and photo-induced electron-hole pair separation. The photocatalysis by TiO_2 NPs for MO degradation under UV light irradiation is exhibited in Figure 7. The photocatalytic activity of MO is 81%, 63.62%, 70.23%, 76.85%, 83.46%, 99.93% and 93.38% for P25, TU0, TU1, TU2, TU3, TU4 and TU5, respectively, under UV light irradiation within 100 min. It can be found that TU4 shows the highest performance and nearly 99.93% decomposition, whereas the P25 exhibits lower photocatalytic activity (81%) within 100 min. Nevertheless, the TU0 sample shows lower photocatalytic activity (63.62%), which is attributed to the aggregated morphology and fast recombination of photoinduced electron-hole pair. It can be seen that the photodegradation efficiency increased with the increasing concentration of precursor urea due to the improved surface morphology and effective electron-hole pair separation. However, further increased concentration of urea led to a decrease in photodegradation efficiency. The excess urea would change the surface morphology of TiO_2 photocatalyst. Therefore, to get maximum photodegradation efficiency, it is essential to optimize the concentration of urea during the synthesis of TiO_2 photocatalyst. It was evident from the present study that the optimum concentration of urea in the TU4 sample offered the highest photodegradation efficiency, where morphology and size of TiO_2 particles are well preserved and have good adsorption ability and effective photoinduced electron-hole pair separation under UV irradiation. The comparisons of reported photocatalytic activity of TiO_2 NPs prepared by different methods are summarized in Table S2. Obviously, the TiO_2 NPs synthesized from the thermal decomposition method exhibited better photocatalytic activity for the photodegradation of MO under UV-light than the sol-gel and hydrothermal method [27,28].

Figure 7. Photocatalytic activity of MO solution over TU4 under UV light irradiation: (a) Absorbance against wavelength; (b) Degradation against Irradiation time.

The most significant criteria for being an excellent photocatalyst in practical application are its photocatalytic activity and stability. To determine the stability of the TU4 photocatalyst, various recycling experiments were undertaken for the photodegradation of MO under UV light. After each set, the photocatalyst was filtered and washed with distilled water, and fresh MO solution was taken for the next set. As shown in the photocatalysis for MO over TU4 photocatalyst (Figure 8), after five recycling experiments, it did not show

a significant decrease in its activity. It was observed that the MO photodegradation activity dropped by up to 5% after five successive cycles. The results show the good stability of TU4 photocatalyst to cater to the need for practical utilities.

Figure 8. Reusability of the TU4 for MO degradation under UV light irradiation.

Based on the obtained results, the detailed plausible mechanism for the photodegradation of MO dye pollutants using TiO_2 is presented in Scheme 1. Due to UV light irradiation, a high-energy photon renders excitation of an electron from the valence band to the conduction band (CB) of TiO_2 , leaving a hole behind in the valence band (VB). Consequently, photogenerated electrons in the CB of TiO_2 react with chemisorbed oxygen molecules to form superoxide radical ($-\text{O}_2^-$). Photoinduced holes had a tendency to react directly with adsorbed water molecules or surrounding hydroxyl groups and generated hydroperoxyl radicals ($-\text{OH}$). Both superoxide radical ($-\text{O}_2^-$) and hydroperoxyl radicals ($-\text{OH}$) play a significant role in degrading the adsorbed MO dye molecules [29]. These radicals degrade the pre-concentrated molecules of MO dye into carbon dioxide and water.

Scheme 1. A Plausible mechanism for the photocatalytic degradation of MO over the TU4 under UV light irradiation.

The effect of scavenger on the rate of photodegradation was studied to determine the roles of the active species responsible for photodegradation of MO over TiO_2 photocatalyst, and the results are depicted in Figure 9. 1,4-Benzoquinone (BQ), iso-propanol (IPA) and ethylene diamine tetra acetic acid (EDTA) acts as the scavengers of the superoxide radical, hydroxyl radical and hole, respectively [30]. It is vivid that in the presence of EDTA, a reasonable decrease in photodegradation (up to 71.23%) was observed, and in the presence of IPA, a considerable decrease in photodegradation (up to 29.31%) was observed. In the presence of BQ, a marginal decrease in photodegradation (up to 26.11%) was observed. Therefore, superoxide radical and hydroxyl radical are the leading active species in the photodegradation of dye.

Figure 9. Effects of different scavengers on the photodegradation of MO in the presence of the TU4 under UV light.

4. Conclusions

We have successfully established an innovative approach for the synthesis of TiO_2 NPs via simple thermal decomposition of titanium oxysulphate and urea with various weight ratios. The strategy reported here is, simple, sustainable, cost-effective and does not use any multi-step procedures. This study demonstrated the use of TiO_2 NPs for the photodegradation of MO as an exemplary pollutant under UV light. As-prepared TiO_2 NPs (TU4) displays significant photodegradation efficiency (99%) compared to pure TiO_2 (TU0) (44%). TiO_2 NPs were also stable enough to be easily recycled without losing their efficiency for up to five consecutive cycles. Such improved photodegradation efficiency was due to controlled aggregation, and the size of TiO_2 NPs has been achieved by using urea and efficient charge separation of photo-induced electron–hole pairs. The previous synthetic method suffers from drawbacks such as the use of toxic substrates, high-cost equipment, high temperature, complicated procedures and low yields. As compared to these synthetic methods, the thermal decomposition method is the relatively fast, simple, cost-effective and environmentally friendly path for large-scale synthesis of TiO_2 NPs. We believe that our synthetic approach for the synthesis of TiO_2 NPs is not only the simplest approach but will also be useful for large-scale production of TiO_2 -based metal oxide nanocomposite with improved photocatalytic activity and will significantly facilitate the elimination of the organic dye pollutants from wastewater.

Supplementary Materials: The following are available online at <https://www.mdpi.com/2079-6412/11/2/165/s1>, Table S1: Various structural parameters of TiO₂ obtained from XRD analysis, Table S2: Comparison of photodegradation performance of TiO₂ with reported photocatalysts.

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