Optimising the crystallinity of anatase TiO$_2$ nanospheres for the degradation of Congo red dye

M. Malligavathy, S. Iyyapushpam, S. T. Nishanthi and D. Pathinettam Padiyan
Department of Physics, Manonmaniam Sundaranar University, Tirunelveli, India

ABSTRACT
Anatase TiO$_2$ nanospheres having a high degradation efficiency are prepared through hydrothermal method employing titanium (IV) isopropoxide as precursor. The effects of hydrothermal temperature on structural, morphological and optical properties of TiO$_2$ nanospheres are investigated. X-ray diffraction (XRD) results show that, the TiO$_2$ nanospheres crystallise in the anatase phase, the tetragonal crystal system. The crystallite size increases with the increase in hydrothermal temperature and the values are in the range of 10–19 nm. On the other hand, the spherical particles evenly distributed on the surface are observed in the scanning electron microscope (SEM) images. The band gap of the nanospheres is determined from the reflectance spectra using Kubelka–Munk function. The band gap energy decreases from 3.189 (2) to 3.023 (5) eV with the increase in hydrothermal temperature. The decrease in band gap values well agree with the XRD results of higher crystallite size and enhanced crystallinity. The removal of Congo red dye under dark condition varies with the hydrothermal temperature and it is maximum for the higher crystallinity anatase TiO$_2$ synthesised at 160°C having a lower band gap of 3.023 (5) eV. Maximum efficiency of 96.9% and rate constant value of 0.01413 g mg$^{-1}$ min$^{-1}$ are observed for the sample hydrothermally synthesised at 160°C.

1. Introduction
Titanium dioxide is a n-type semiconducting material with tetragonal crystal structure and it has received a great deal of attention due to their many applications, such as photo catalytic activity,[1] gas sensor,[2] dye sensitised solar cells [3] and water splitting.[4] Anatase is one of the crystalline polymorphs (anatase, rutile and brookite) of TiO$_2$. It is generally more active than rutile phase for photo catalytic applications.[5] The properties of TiO$_2$ depend on many parameters like crystal phase, nanoparticle size and morphology.[6] Many methods such as sol-gel,[2] hydrothermal,[7] hydrolysis [8] and microwave assisted hydrothermal method [9] had been used to prepare TiO$_2$ nanoparticles. However, in this present work, hydrothermal method is chosen because it has various advantages like producing crystalline products at lower temperature and prevents agglomeration.
between particles. Erdemoglu et al. [11] prepared TiO₂ nanoparticles by hydrothermal method at the temperature of 200 °C for 2 h and studied its photo catalytic degradation of Congo red (CR) by varying the wt% of TiO₂. They attain 93.9% efficiency for 0.25 wt% of TiO₂ after the visible light irradiation for 30 min. Farbod et al. [12] prepared TiO₂ nanopowders by sol-gel milling process and they achieved 50% degradation of CR in 60 min for the 650 °C annealed samples. Hong et al. [13] prepared titania/sulphanilic acid by hydrothermal method at 160 °C for 10 h and reported that CR completely degraded in 210 min under visible light. Gupta et al. [14] have used different adsorbents such as bottom ash (a power plant waste), de-oiled soya (an agricultural waste), blast furnace slag, dust and sludge for removal of phenol red, chrysoidine Y, triarylmethane, light green, crystal violet, meldola blue, chrysoidine G. Heterogeneous catalyst (Fenton’s reagent and mesoporous activated carbon) were used to degrade aniline and the degradation was confirmed using Fourier transform infrared spectroscopy (FT-IR), nuclear magnetic resonance spectroscopy (NMR) and ultraviolet-visible (UV-Vis) spectroscopy. Several adsorbents have been used for the removal of heavy metals like Pb, Hg, Cr and Cd. Alumina coated carbon nanotubes, CNT/magnesium oxide and activated carbon (from fertiliser waste) and Fe₂O₃ nanoparticles were used in removal of lead, copper and cadmium respectively. Other than waste material adsorbents, CNT and activated carbon were also used to remove methylene blue, reactive red and copper ions from the waste water. Mittal et al. [26] studied the adsorptive removal of CR dye using waste materials (bottom ash and de-oiled soya) and they achieved 96.95% in 250 min using 0.05 g/25 ml. Gupta et.al explained the removal of tartrazine and amaranth dye by photo catalytic degradation on the surface of titanium dioxide. Under dark conditions, no absorption takes place for both the dyes, but the presence of UV light strongly affects the photo degradation of TiO₂. Saleh [29] reported 65% efficiency in 100 min for methyl orange with a catalyst amount of 10 mg/50 ml of TiO₂ (irradiated using UV light). To the best of our knowledge, there are no reports on the use of pure TiO₂ nanospheres for the degradation of CR without light, i.e. under dark condition.

The aim of the present work is to prepare phase pure anatase TiO₂ nanospheres at various hydrothermal temperatures and to analyse its degradation efficiency for CR without light irradiation. The effects of hydrothermal temperature on the degradation of the pollutant are determined using pseudo first and second order kinetics.

2. Experimental details

2.1 Materials used

Titanium (IV) isopropoxide (Sigma Aldrich), ethanol, glacial acetic acid (Merck) and CR (Sigma Aldrich) were purchased and used for the sample preparation. Double distilled water was used throughout the experiment.

2.2 Preparation

TiO₂ nanospheres were prepared by a hydrothermal treatment. Five millilitres of titanium (IV) isopropoxide (Ti(OCH₃H₇)₄) was taken in a beaker and 10 ml of ethanol was added drop by drop under constant stirring. To this solution, 20 ml of double distilled water was
added dropwise and stirred for 30 min. Then, 5 ml of glacial acetic acid was added to the above solution (pH = 3). Now, the resulting solution was transferred into a 50 ml Teflon-lined stainless steel autoclave and hydrothermally treated at 100 °C in an oven for 24 h. Finally, the autoclave was cooled to room temperature, and the precipitate was centrifuged and washed several times using double distilled water. The resulting precipitates were dried overnight in an oven at 80 °C and the sample was named as S1. Similarly, the samples were hydrothermally treated at different temperatures 120, 140, 160 and 180 °C for 24 h and named as S2, S3, S4 and S5, respectively.

2.3 Characterisation

X-ray diffraction (XRD) was performed on a PANalytical XPERT-PRO X-ray diffractometer with CuKα (λ = 1.5406 Å) as an incident radiation. The accelerating voltage and current were 40 kV and 30 mA, respectively. The surface morphology and composition of the nanospheres were observed by a high resolution scanning electron microscope (HR-SEM) (FEI Quanta FEG 200) equipped with an energy dispersive X-ray spectroscopy (EDX). Shimadzu UV-2700 diffuse reflectance spectrophotometer (DRS) was used to obtain reflectance spectra in the wavelength region 220—850 nm using BaSO4 powder as reference. CR was chosen as a model pollutant for degradation studies using TiO2 as a catalyst. The removal of the dye CR was studied for every 15 min using fresh samples of TiO2 nanospheres under dark condition and the residual concentration of the dye in the solution was obtained using UV-Vis spectrophotometer (Techcomp, UV 2301) in the range of 200—900 nm.

3. Results and discussion

3.1 Structural properties

The XRD patterns of TiO2 nanospheres of S1, S2, S3, S4 and S5 shown in Figure 1 evidence the polycrystalline nature of the samples. It should be noted that only anatase peaks can be detected and no rutile or brookite phase is found in the XRD pattern. All the XRD peaks are matched well to anatase phase of TiO2 and the peaks are in agreement with the reference pattern Joint Committee on Powder Diffraction Standards (JCPDS) Number 71-1167 of TiO2. From this, it is clearly confirmed that, the formed system crystallises in tetragonal structure. From the figure, it is evident that the intensity of (1 0 1) plane increases with the increase in hydrothermal temperature up to S4 and then it decreases for S5. The crystallite size (D) of the TiO2 is calculated using the Scherrer formula [30] given by

\[ D = \frac{K\lambda}{\beta \cos \theta} \]  

where K → Scherrer constant (= 0.9), \( \lambda \) → wavelength of X-ray used, \( \beta \) → full width at half maximum and \( \theta \) → scattering angle. The crystallite size is determined by considering the first three prominent peaks and its average value is given in Table 1.

Here, also the crystallite size increases with the increase in hydrothermal temperature and decreases for the sample S5. The cell constants and cell volume are calculated from the unit cell software and is given in Table 2 for comparison.
In general, it is observed that the volume of the unit cell shrinks slightly with the increase in hydrothermal temperature and it may be due to the increasing pressure developed at higher temperatures.

Figure 2 shows the HR-SEM image of TiO$_2$ nanospheres prepared at various hydrothermal temperatures. From the figure, it is clear that smooth spherical particles seen on

Table 1. Crystallite size and band gap of TiO$_2$ nanospheres.

| Sample | XRD Crystallite size (nm) | DRS Band gap (eV) |
|--------|---------------------------|-------------------|
| $S_1$  | 10.8                      | 3.189 (2)         |
| $S_2$  | 11.0                      | 3.176 (2)         |
| $S_3$  | 16.8                      | 3.064 (2)         |
| $S_4$  | 19.5                      | 3.023 (5)         |
| $S_5$  | 12.5                      | 3.053 (4)         |
the surface and the particle sizes are small. The distribution of the particle is uniform and the particle size lies between 13 and 19 nm. The value of particle size observed from scanning electron microscope (SEM) is in good agreement with the results obtained from XRD. With the increase in hydrothermal temperature, the samples possess well-defined shapes and larger particle size. The EDX analysis indicated the presence of Ti and O in TiO₂ nanoparticles. No other impurity peaks are observed in EDX confirming the purity of the sample.

| Sample | \(a = b\) (Å) | \(c\) (Å) | Cell volume (Å\(^3\)) |
|--------|---------------|------------|-----------------------|
| S₁     | 3.8235 (1)    | 9.4634 (7) | 138.35 (1)            |
| S₂     | 3.8119 (1)    | 9.4297 (7) | 137.02 (1)            |
| S₃     | 3.8151 (2)    | 9.4689 (7) | 137.82 (1)            |
| S₄     | 3.8167 (1)    | 9.4602 (7) | 137.81 (1)            |
| S₅     | 3.8038 (1)    | 9.4475 (7) | 136.69 (1)            |

**Figure 2.** HR-SEM micrograph for TiO₂ nanospheres of (a) S₁, (b) S₂, (c) S₃, (d) S₄ and (e) S₅.
3.2 Optical properties

The optical reflectance of all the five samples of TiO₂ is investigated using DRS at room temperature, and is shown in Figure 3. The reflectance spectra of the TiO₂ nanoparticles show a red shift with the increase in hydrothermal temperature. All the samples exhibited absorption in the UV region at 350–400 nm which is due to the charge transfer from the valence band (2p orbital) to the conduction band (3d orbital) [31] and the absorbance spectra is shown as an inset in Figure 3. The band gap value of the sample was calculated using Kubelka—Munk function [32]

\[ F(R_\infty) = \frac{(1 - R_\infty)^2}{2R_\infty} \]  
(2)

where \( R_\infty = \frac{R_{\text{sample}}}{R_{\text{standard}}} \). \( R_{\text{sample}} \) is the reflectance of the sample and \( R_{\text{standard}} \) is the reflectance of the BaSO₄ (reference) sample. The equation relating band gap (\( E_g \)) and absorption coefficient (\( \alpha \)) is

\[ \alpha = \frac{(h\nu - E_g)^n}{h\nu} \]  
(3)

where \( h\nu \) is the energy of the incident photon and \( n \) depends on the type of transition (1/2 for direct and 2 for indirect). For indirect transition, the Equation (2) becomes, [\( F(R_\infty) h\nu \)]^{1/2} = \( A(h\nu - E_g) \), where \( A \rightarrow \) proportionality constant. The indirect band gap measured from the plot of [\( F(R_\infty) h\nu \)]^{1/2} vs. photon energy is shown in Figure 4. The band gap was obtained by extrapolating the linear part to zero on the ordinate axis. The band gap values obtained are 3.189 (2), 3.176 (2), 3.064 (2), 3.023 (5) and 3.053 (4) eV for S₁, S₂, S₃, S₄ and S₅, respectively. It has been observed that the band gap decreases with the increase in hydrothermal temperature up to S₄ and then slightly increases for S₅. The decrease in band gap values well agrees with the XRD results of higher crystallite size and enhanced crystallinity.

Figure 3.(Colour online). Reflectance spectra for TiO₂ nanospheres of (a) S₁, (b) S₂, (c) S₃, (d) S₄ and (e) S₅, and the inset figure shows the absorption spectra.
3.3 Removal of Congo red

CR was chosen as a model pollutant with a concentration of 10 ppm. 10 mg of TiO$_2$, the catalyst was dispersed in 50 ml of CR solution. The solution was magnetically stirred in the dark condition at room temperature and the concentration of CR dye was measured for every 15 min using UV-Vis spectrophotometer. For every 15 min, 10 ml of suspension was taken out, centrifuged for 10 min and the solution was separated for measurement. The absorbance spectra of CR shown in Figure 5 have two characteristic peaks in the visible region one at 498 nm and the other band at 338 nm and are attributed to the azo bond (-N$_2$N-) and naphthalene ring structure of CR dye,[33] respectively. During degradation, the absorbance value decreases with time and it is due to the breakup of chromophore bonds in CR dye. The removal efficiency of catalysts for CR dye after various intervals of time is calculated using the equation,

$$\text{Removal efficiency} \, (\%) = \frac{(\text{Abs}_0 - \text{Abs}_t)}{(\text{Abs}_0)} \times 100\% \quad (4)$$

where $\text{Abs}_0$ is the initial absorbance and $\text{Abs}_t$ is the absorbance after time $t$. The absorption spectra shown in Figure 5 reveal the decrease of concentration with time in all the samples, and in that the sample, $S_4$ shows the maximum removal efficiency in 90 min. The removal efficiency of the present work is compared with the reported values and is given in Table 3.[34–44] Most of the results show that, the pure TiO$_2$ samples degrade CR under UV or visible light with higher catalyst amount and irradiation time. However, in the present work, the phase pure anatase TiO$_2$ nanospheres removes 96.9% of CR within 90 min using 10 mg of catalyst under dark condition. The amount of dye adsorbed per unit ($q_e$) was calculated using the
Figure 5. (Colour online). Removal of Congo red using TiO$_2$ nanospheres (a) S$_1$, (b) S$_2$, (c) S$_3$, (d) S$_4$ and (e) S$_5$, and the inset shows the pseudo first order kinetics.
The following equation:

\[ q_e = V (C_i - C_f) / m \]  

(5)

where \( V \) is the volume of the dye solution (ml), \( C_i \) and \( C_f \) are the initial and final concentration (mg l\(^{-1}\)) of the dye, respectively, and \( m \) is the weight of the catalyst (g). The \( q_e \) value obtained from the experiment is given in Table 4.

The removal of CR dye by TiO\(_2\) nanospheres is analysed using pseudo first and pseudo second order kinetics.

### Table 3. Comparison in degradation of Congo red using TiO\(_2\).

| Catalyst            | Synthesis method | Medium | Removal conditions                                                                 | Ref. |
|---------------------|------------------|--------|------------------------------------------------------------------------------------|------|
| TiO\(_2\)           | Sol-gel          | Light  | Catalyst amount: 250 mg/100 ml Irradiation time: 5 h (UV light) Efficiency: 100%  | [34] |
| TiO\(_2\) nanorods  | Low temperature method | Light  | Catalyst amount: 0.1 g/80 ml Irradiation time: 35 min (sun light) Efficiency: 100% | [35] |
| TiO\(_2\) powder    | —                | Light  | Catalyst amount: 0.05 g/50 ml (10 ppm) Irradiation time: 180 min (ultrasonic) Efficiency: 100% | [36] |
| P25 TiO\(_2\)       | —                | Light  | Catalyst amount: 0.15 g/100 ml (40 ppm) Irradiation time: 210 min (visible) Efficiency: 12% | [37] |
| TiO\(_2\)           | —                | Light  | Catalyst amount: 25 mg/200 ml (20 ppm) Irradiation time: 120 min (UV-Vis) Efficiency: 55% | [38] |
| TiO\(_2\) nanoparticles | Sol-gel        | Light  | Catalyst amount: 1 g/l (20 ppm) Irradiation time: 210 min (UV light) Efficiency: 80% (particle size – 55 nm) | [39] |
| TiO\(_2\) P25       | —                | Light  | Catalyst amount: 0.08 g/500 ml Irradiation time: 6 h (UV light) Efficiency: dark: 18.6% and UV: 85.9% | [40] |
| TiO\(_2\) P25       | —                | Light  | Catalyst amount: 1 g/l (55 ppm) Irradiation time: 480 min (UV light) Efficiency: 90% | [41] |
| TiO\(_2\) nanoparticles | Sol-gel        | Light  | Catalyst amount: 0.1 mg/ml in 20 ml Irradiation time: 600 min (UV light) Efficiency: 60% (particle size – 50 nm) | [42] |
| TiO\(_2\) P25       | —                | Light  | Catalyst amount: 0.5 g/l in 100 ml (20 ppm) Irradiation time: 240 min (UV light) Efficiency: 90% | [43] |
| TiO\(_2\) P25       | —                | Light  | Catalyst amount: 0.05 g/200 ml (10 ppm) Irradiation time: 170 min (visible) Efficiency: 27% | [44] |
| TiO\(_2\) nanospheres | Hydrothermal    | Dark   | Catalyst amount: 10 mg/50 ml (10 ppm) Time: 90 min Efficiency: 96.9% | Present work |

### Table 4. Pseudo first and second order kinetics parameters of TiO\(_2\) for CR dye removal.

| Sample | Efficiency (%) | \( q_e \) (mg/g) (from experiment) | \( k_1 \) (min\(^{-1}\)) | \( R \) | \( q_e \) (mg/g) (from graph) | \( k_2 \) (g mg\(^{-1}\) min\(^{-1}\)) | \( R \) |
|--------|----------------|-----------------------------------|--------------------------|--------|-------------------------------|---------------------------------|--------|
| \( S_1 \) | 93.9           | 47.35                             | 0.028 (5)                | 0.9225 | 48.08                         | 0.00760                         | 0.9985 |
| \( S_2 \) | 94.4           | 47.35                             | 0.028 (5)                | 0.9030 | 48.08                         | 0.00840                         | 0.9989 |
| \( S_3 \) | 96.2           | 48.11                             | 0.029 (6)                | 0.8952 | 48.31                         | 0.0109                          | 0.9992 |
| \( S_4 \) | 96.9           | 48.13                             | 0.032 (7)                | 0.8738 | 48.75                         | 0.01413                         | 0.9996 |
| \( S_5 \) | 96.2           | 46.98                             | 0.027 (6)                | 0.8743 | 47.84                         | 0.01716                         | 0.9995 |
3.3.1 Kinetics of CR dye removal

According to Langmuir–Hinshelwood model, when the initial concentration $C_0$ is very small, the equation is given by [45]

$$\ln\left(\frac{C_0}{C_t}\right) = kt$$

(6)

where $k \rightarrow$ pseudo first order rate constant and $C_t$ is the concentration at time $t$. The variations in $\ln\left(\frac{C_0}{C_t}\right)$ as a function of time is shown in Figure 5 as inset. The removal efficiency, first order kinetic rate constant ($k$) and regression coefficient ($R$) are given in Figure 6.

Figure 6.(Colour online). Langmuir–Hinshelwood pseudo second order kinetics for the removal of Congo red using TiO$_2$ nanospheres of (a) $S_1$, (b) $S_2$, (c) $S_3$, (d) $S_4$ and (e) $S_5$. 
Table 4. Since, the regression coefficient is not nearly equal to 1, in the present work, pseudo second order kinetics was tried. Blanchard [46] presented the pseudo second order as

\[ q_t = \frac{(k_2 q_e^2 t)}{(1 + k_2 q_e t)} \]

where \( q_e \) and \( q_t \) are the amount of dye adsorbed at equilibrium and at time \( t \) (mg/g) and \( k_2 \) is the pseudo second order rate constant (g mg\(^{-1}\) min\(^{-1}\)). The obtained equation can be rearranged into a linear form as, \( t/q_t = t/q_e + 1/k_2 q_e^2 \). A plot between \( t/q_t \) versus time (Figure 6) gives the value of \( q_e \) (mg/g) and \( k_2 \) (g mg\(^{-1}\) min\(^{-1}\)) calculated, and is given in Table 4 for comparison. The regression coefficient values are nearly equal to 1 and exhibit the pseudo second order fitting.

The observed crystallite size increases with the decrease in the band gap, and has a direct relation of the increase in removal efficiency. For a good catalytic activity, the rate of electron-hole recombination should be minimum and it is also known that higher crystallinity lowers the charge carrier recombination rate.[47] The efficiency increases with hydrothermal temperature and S₄ shows the highest removal efficiency of CR. This is attributed to the larger crystallite size and the lower band gap of S₄ compared to other samples.

4. Conclusions

Anatase phase TiO₂ nanospheres have been successfully prepared by hydrothermal method. The effect of temperature on the preparation of TiO₂ nanospheres was studied in the range of 100–180 °C. Anatase phase was observed in all temperature with the crystallite size was found to vary inversely to the energy band gap. With the increase in hydrothermal temperature up to 160 °C, the crystallinity is improved and the band gap shifted towards the visible region. Beyond this optimum level, both the crystallinity and the band gap changes result in lower removal efficiency. The pseudo second order kinetics fits well for the whole range of degradation time and the removal efficiency is maximum for the sample treated at 160 °C with a higher correlation coefficient. This study provides a simple and inexpensive way to prepare highly active anatase TiO₂ which degrade CR quickly in 90 min.

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Disclosure statement

No potential conflict of interest was reported by the authors.

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