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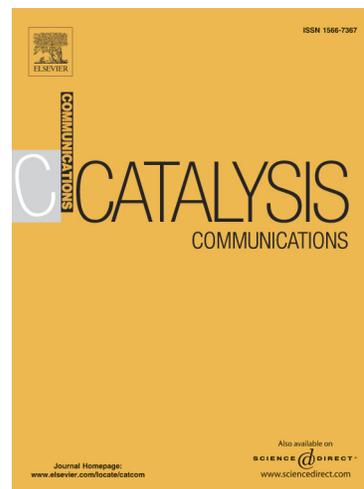
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**Synthesis of nanocrystalline titania by hydrothermal method using cetyl pyridinium chloride as a template and its catalytic applications**

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**Abstract:**

Nano crystalline titanium dioxide predominantly in the anatase phase has been synthesized from titanium isopropoxide by dispersion technique using hydrothermal synthesis method in water-ethanol system. The material was characterized for its structural and textural properties using powder X-ray diffraction (XRD), TG-DTA, transmission electron microscopy (TEM) and by low temperature N<sub>2</sub> adsorption at 77K. Both TEM and XRD data reveal a uniform and nanocrystalline TiO<sub>2</sub> particles of 8 and 14 nm for the as synthesized and calcined samples respectively. The calcined sample showed photo catalytic activity in the decomposition of methylene blue in aqueous medium under both UV and visible light region. The results are compared with degussa P-25 TiO<sub>2</sub> sample.

**Keywords:** TiO<sub>2</sub>, nanocrystalline, Anatase, photocatalytic activity, Methylene blue

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## 1. Introduction

The three crystalline polymorphs of titania are anatase, brookite and rutile. Among these polymorphs, anatase-TiO<sub>2</sub> is important phase as it attracts more attention for its use as pigments [1], gas sensors [2] and catalysts [3]. Due to its semiconducting activity, TiO<sub>2</sub> is used as photo catalysts [4] in environmental related problems of pollution control. Other than these, titania powders are widely applicable as fillers and opacifiers. It is well known nowadays that nanostructured materials are having higher active surfaces, which make them preferred than the macroporous materials. Among the various methods of preparing nanostructured TiO<sub>2</sub>, co-precipitation, sol-gel, hydrothermal routes, ultra-sonication etc. are popular. [5-7]. Colloidal chemistry has offered the means for fabrication of nanoparticles. One of them is reverse-micelle synthesis that helps in tailoring size and shape of the particles [8]. In the present work, we have employed surfactant assisted hydrothermal synthesis of TiO<sub>2</sub> nanoparticles of uniform size.

In the present study nanocrystalline anatase titania was synthesized using a template, cetyl pyridinium chloride by hydrothermal synthesis and characterized it by different techniques such as XRD, TEM, BET surface area and thermogravimetry. The synthesized anatase titania was tested for the photo catalytic decomposition of methylene blue (MB) in aqueous medium under both UV and visible light and compared with the data on degussa TiO<sub>2</sub>.

## 2. Experimental

### 2.1 Synthesis

Nanocrystalline titanium dioxide has been synthesized from titanium isopropoxide by dispersion technique using hydrothermal synthesis method in water-ethanol system. Cetylpyridinium chloride has been used as the surfactant. Cetylpyridinium chloride was dispersed previously in ethanol and titanium isopropoxide was added to it. Precautions were taken to avoid hydrolysis of titanium isopropoxide during addition. Hydrolysis of the reaction mixture was done by adding water. Finally the molar ratio of water: ethanol was 1:2. Resultant gel was transferred to a teflon lined autoclave. Hydrothermal synthesis was carried out under autogenous pressure at 180°C for 7 days. Resulting powder was washed thoroughly with ethanol and dried at 120°C overnight. As synthesized TiO<sub>2</sub> was calcined at 500°C for 6 hours to remove surfactant used in the synthesis.

## 2.2 Characterization

Powder X-ray diffraction patterns of the as synthesized and calcined samples were taken using a Rigaku D-Max III VC Powder XRD diffractometer. Ni filter was used to suppress the CuK<sub>β</sub> radiation, and NaI scintillation counter as detector. The patterns were collected in the range 20–80° 2θ with a speed of 2°/min in the continuous scan mode. The peak width (FWHM) of the XRD profile was determined using the equation,  $FWHM = \sqrt{u + v \tan\theta + w \tan^2\theta}$  and then the crystallite size (L) was determined using the Scherrer equation [9],  $D = k\lambda/\beta\cos\theta$ , where D is the crystallite size, k is the Scherrer constant (= 0.9 assuming that the particles are spherical), λ is the wavelength of the X-ray radiation (Cu K<sub>α1</sub> radiation, λ = 1.5406 Å), β is the line width (obtained after correction for the instrumental broadening is applied) and θ is the diffraction peak angle. TEM measurements were carried out on a JEOL Model 1200EX instrument operated at an

accelerating voltage of 100 kV. The fine powders were dispersed in isopropanol on a carbon coated TEM copper grid. The thermogravimetric analysis of the as synthesized TiO<sub>2</sub> was carried out to monitor the nature of decomposition of surfactant. Thermal analysis was done on a Setaram thermal analyzer (SETARAM) at a heating rate of 10° min<sup>-1</sup> in air atmosphere. BET surface area was measured by N<sub>2</sub> adsorption–desorption isotherm at liquid nitrogen temperature using Autosorb-3B (Quantachrome, USA). Prior to the adsorption–desorption measurements, sample was degassed at 300°C in N<sub>2</sub> flow for 16 h.

### 2.3 Photocatalytic activity

The photocatalytic oxidation experiment were carried out in a photoreactor with a capacity of 250 ml. 23 mg of TiO<sub>2</sub> sample was dispersed in 230 ml of 10 ppm (aqueous) MB dye solution. The reaction mixture was stirred with a magnetic stirrer. It was then photo-irradiated at room temperature by using a 450-Watt, mercury vapour lamp (Hanovia). The photocatalytic degradation of methylene blue in the visible region was carried out at room temperature using a 500-Watt sodium vapour lamp. The decomposition of methylene blue dye was monitored by UV-Vis spectrophotometer. (Shimadzu 2101PC,  $\lambda_{\text{max}} = 665 \text{ nm}$ ), at regular intervals of time. The photocatalytic reaction procedure was repeated for TiO<sub>2</sub> (Degussa) standard sample.

## 3. Results and discussion

### 3.1 Powder X-Ray diffraction

The powder XRD patterns of as synthesized and calcined TiO<sub>2</sub> samples are shown in Fig. 1. All the peaks observed in the XRD patterns belong to anatase as well as

brookite phase of  $\text{TiO}_2$  (marked as A and B respectively). The calculated lattice parameters for anatase are  $a=3.784 \text{ \AA}$  and  $c=9.514 \text{ \AA}$ . The phase composition of anatase was found to be 86%. The average crystallite size of as synthesized and calcined  $\text{TiO}_2$  was estimated by the FWHM was 8 and 14 nm, respectively.

### 3.2 TG-DTA and low temperature $\text{N}_2$ adsorption studies

The TG and DTG of the as synthesized  $\text{TiO}_2$  are shown in Fig. 2. The total weight loss measured from the TG curve was 38.43 wt%. While the weight loss (2.94% wt) in the range 80-120°C can be attributed to the removal of water, the decomposition of surfactant cetylpyridinium chloride was observed between 250-310°C (35.49% wt. loss). The TG curve shows that weight loss saturated at 500°C and hence the minimum calcination temperature for complete removal of the organic surfactant molecules is around 500°C.

The measured BET surface area of the calcined  $\text{TiO}_2$  powder was found to be 89  $\text{m}^2/\text{g}$ . Considering the density of anatase titania as  $3.9 \text{ g cm}^{-3}$  and assuming the particles to be spherical, the average particle size from the surface area correspond to particles with a mean diameter of about 17 nm which is marginally more than that determined by XRD (14nm). There seems to be not much agglomeration of particles in the calcined sample.

### 3.3 Transmission Electron Microscopy

Fig. 3a and 3b show typical TEM micrographs of as the synthesized and calcined  $\text{TiO}_2$  respectively. It can be seen that as synthesized and calcined  $\text{TiO}_2$  has a uniform distribution of  $\text{TiO}_2$  particles of ~8nm and 14 nm in size respectively. The agreement in the particle size by TEM and crystallite size by XRD indicates that there is no

agglomeration of particles of  $\text{TiO}_2$  as observed earlier for reverse micelle synthesis [8] and microwave-assisted synthesis [10].

### 3.4 Photo-catalytic decomposition of methylene blue in the UV region

The photo catalytic activity of the titania sample under UV light is compared with commercial Degussa P-25 sample, having surface area  $50 \text{ m}^2 \text{ g}^{-1}$  and particle size 30 nm. Fig. 4a and b shows the UV-Visible absorption data on the gradual decrease in the concentration of MB over  $\text{TiO}_2$  and  $\text{TiO}_2$ -Degussa as a function of time respectively. It can be seen that the degradation of MB over the sample prepared by hydrothermal method is comparable with that of Degussa P-25 sample. Fig. 5a depicts the results on the photo-catalytic oxidation of MB in presence of UV light. Period 'a' is the initial time (20 min for all the samples) during which the mixture of sample and methylene blue in water was stirred in dark. Period 'b' denotes the results obtained with time on stream subjecting the mixture for exposure to UV irradiation. A typical run without UV irradiation confirmed that there is no photo-oxidation taking place. From Fig. 5a, it is evident that there is no photo-oxidation in dark (region 'a' for all the samples) except adsorption of small amount of MB on the samples. Decomposition of methylene blue was complete after 150 min of UV irradiation on the calcined  $\text{TiO}_2$ . We have earlier reported the photocatalytic activity on titania prepared by solgel procedure with a crystallite size of 8 nm [3] which is better than this sample although the particles are more homogeneous and dispersed better (see TEM) in the present sample. This is likely due to the quantum size effect caused by the higher crystallite size (14 nm) and also due to the brookite phase present in this sample. It is reported already that the sample prepared by the same sol gel procedure and calcined at 773 K yielded titania of 18 nm, which took 210 min for

complete decomposition of MB [3]. The decrease in crystallite size increases the surface area and thereby increases available average active sites. Decrease in crystallite size also increases higher photo-ionic efficiency from a higher interfacial charge carrier transfer rate. This shows that the photodecomposition activity for MB is higher for smaller crystallite size of pure anatase titania. Although the particles are agglomerated, pure anatase crystallites are better catalysts than the samples having no agglomeration of anatase particles, but presence of brookite impurity.

### ***3.5 Photo-catalytic decomposition of methylene blue in the visible region***

The photo catalytic decomposition of methylene blue on the titania under visible light at ambient temperature is shown in Fig. 5b. For comparison, the performance of Degussa P-25 is also shown. The titania sample shows only 80% degradation of MB after 230 min. of irradiation. The poor photo catalytic activity in comparison to Degussa is likely due to the presence of brookite phase of titania.

## **4. Conclusions**

Nanocrystalline titanium oxide can be effectively prepared by the hydrothermal method using cetyl pyridinium chloride as a template. Anatase is found to be the dominant phase with brookite as a minor phase. As synthesized and calcined  $\text{TiO}_2$  particles are spherical and uniform whose average particle size is ~8 and 14 nm respectively. Both TEM and powder XRD results on particle and crystallite size respectively, agree with each other, which indicates that there is no agglomeration of the crystallites and the particles are well dispersed. The surface area of the calcined  $\text{TiO}_2$  sample was  $89 \text{ m}^2/\text{g}$ . The sample shows good photo catalytic activity for the photodecomposition of methylene blue in aqueous medium under both UV and Visible

light. The material obtained is having good photo catalytic properties comparable to degussa TiO<sub>2</sub> because of its nanosize.

### **Acknowledgements**

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**Legend for figures**

1. Powder XRD patterns of i) as synthesized and ii) calcined TiO<sub>2</sub> sample
2. Thermograms and differential thermograms of as synthesized TiO<sub>2</sub>
3. TEM image of a) as synthesized and b) calcined TiO<sub>2</sub> sample
4. a UV-Visible absorption data on the gradual decrease in the concentration of MB over TiO<sub>2</sub> (Fig. 4 a) as a function of time.
4. b UV-Visible absorption data on the gradual decrease in the concentration of MB over TiO<sub>2</sub>-Degussa (Fig. 4 b) as a function of time.
5. a Decrease in the concentration of MB after photo-catalytic oxidation in presence of UV light.
5. b Decrease in the concentration of MB after photo-catalytic oxidation in presence of visible light.

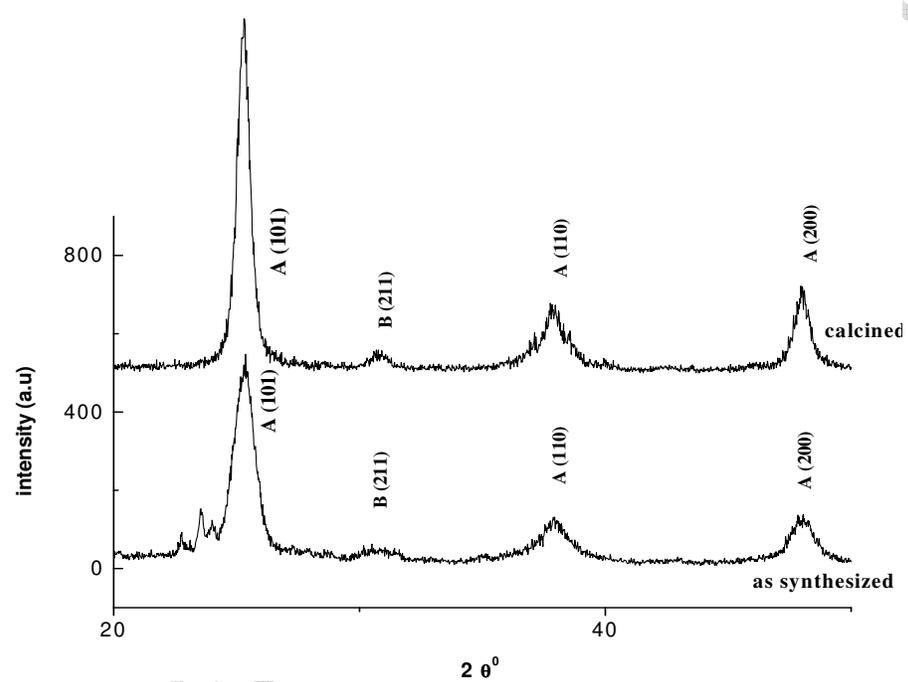


Figure 1

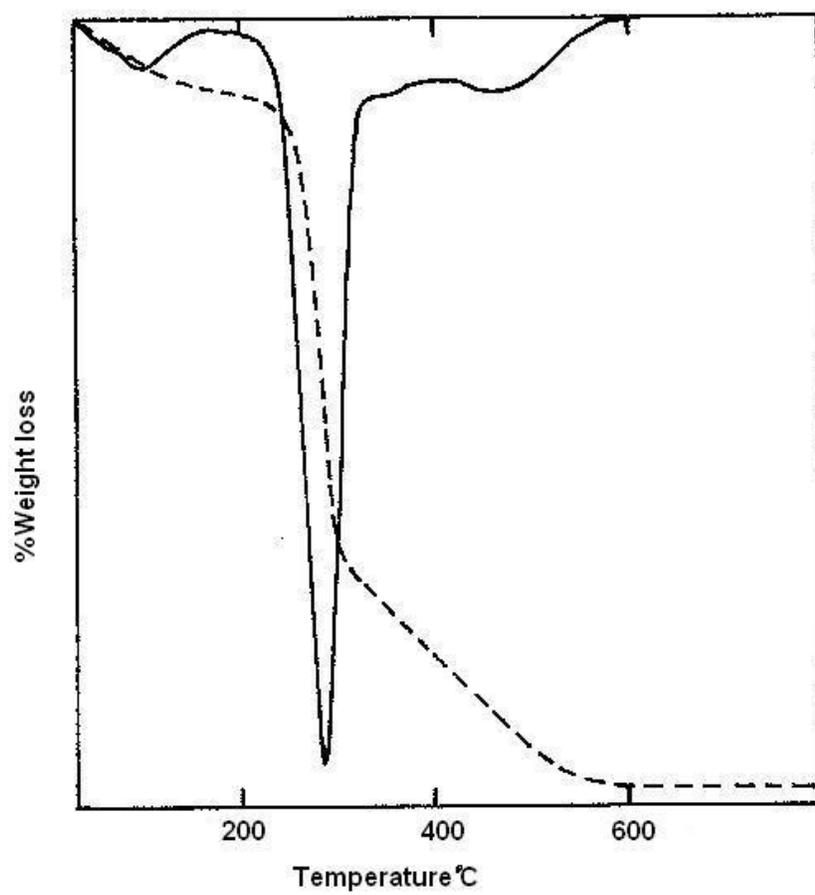
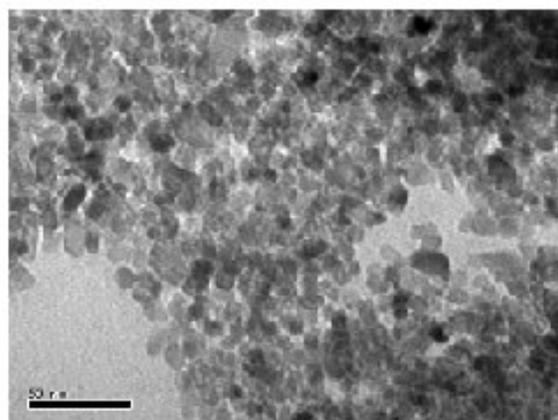
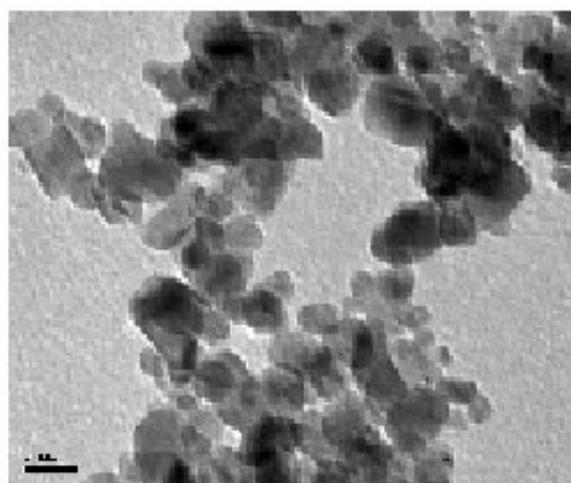


Figure 2



**a**



**b**

Figure 3

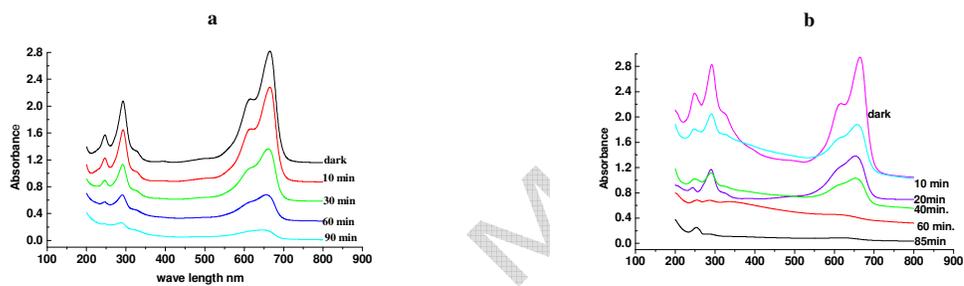


Figure 4

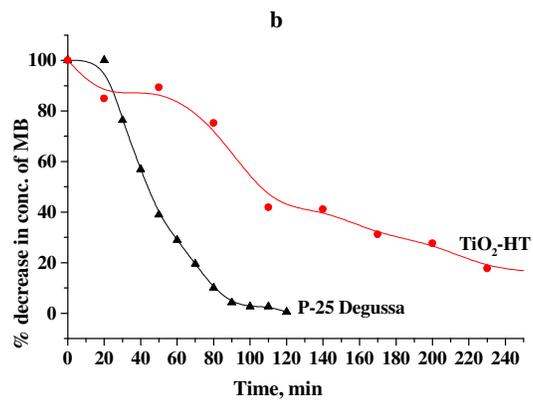
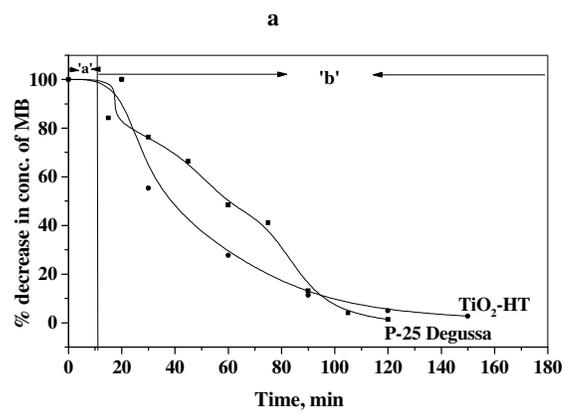


Figure 5