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Photocatalytic degradation of dyes and organic contaminants in water using nanocrystalline anatase and rutile TiO₂

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Abstract

Nanocrystalline TiO₂ was synthesized by controlled hydrolysis of titanium tetraisopropoxide. The anatase phase was converted to rutile phase by thermal treatment at 1023 K for 11 h. The catalysts were characterized by X-ray diffraction (XRD), diffuse reflectance spectroscopy (DRS), Fourier-transform infrared absorption spectrophotometry (FT-IR) and N₂ adsorption (BET) at 77 K. This study compare the photocatalytic activity of the anatase and rutile phases of nanocrystalline TiO₂ for the degradation of acetophenone, nitrobenzene, methylene blue and malachite green present in aqueous solutions. The initial rate of degradation was calculated to compare the photocatalytic activity of anatase and rutile nanocrystalline TiO₂ for the degradation of all substances under ultraviolet light irradiation. The higher photocatalytic activity was obtained in anatase phase TiO₂ for the degradation of all substances as compared with rutile phase. It is concluded that the higher photocatalytic activity in anatase TiO₂ is due to parameters like band-gap, number of hydroxyl groups, surface area and porosity of the catalyst.

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Keywords: Nanocrystalline TiO2; Anatase; Rutile; Band-gap; Hydrothermal method; Photocatalysis; Dyes; Organic compounds

1. Introduction

Contaminants from industrial effluents often pose a major environmental problem. Semiconductor photocatalysis is one technique that has great potential to control aqueous organic contaminants or air pollutants. It holds several advantages over conventional oxidation processes, such as (1) complete mineralization of the pollutants, (2) use of near-UV or solar light, (3) no addition of other chemicals, and (4) operation at near room temperature [1–6]. Although photocatalytic degradations of trace toxic organic compounds in water or air have been investigated intensively in the past decade, there still remain some problems for practical applications [5]. Fundamental research regarding the preparation of photocatalysts with high photocatalytic activity, the immobilization of powder photocatalyst and the improvement of photocatalyst performance are priorities to be considered [5–8]. Among various oxide semiconductor photocatalysts, TiO₂ is an important photocatalyst due to its strong oxidizing power, non-toxicity and long-term photostability. Specific applications of TiO₂ crystalline particles are determined by their chemical, structural and physical properties. In particular, its surface state, the nature and concentration of surfaceactive centers and defects are considered to play important roles. TiO₂ exists in three different crystalline phases: rutile, anatase and brookite, among which rutile is a thermodynamic stable state, while the latter two phases are metastable states [9]. The photocatalytic activity of TiO_2 depends on its phase structure, crystallite size, specific surface areas and pore structure. For example, many studies have confirmed that the anatase phase of TiO_2 is a superior photocatalytic material for air purification, water disinfection, hazardous waste remediation and water purification [1,2]. However, it is not yet well understood which factors are responsible for the higher photocatalytic activity of anatase than rutile TiO₂.

In this work, we synthesized anatase and rutile nanocrystalline TiO_2 and tried to characterize both the

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nanocrystalline TiO₂ phases by X-ray diffraction (XRD), diffuse reflectance spectroscopy (DRS), Fourier-transform infrared absorption spectrophotometry (FT-IR) and BET techniques and determined the photocatalytic activity by degradation of various pollutants. The nanocrystalline anatase and rutile TiO₂ were prepared from the same precursor and by a similar preparation route. The catalytic activity of anatase and rutile TiO₂ catalysts was rationalized in terms of crystallographic phase, surface area, porosity, band-gap and number of hydroxyl groups present in anatase and rutile TiO₂. Some water pollutant substances like acetophenone, nitrobenzene, methylene blue and malachite green were studied in aqueous medium for photocatalytic degradation under irradiation of ultraviolet light.

2. Experimental

2.1. Chemicals and materials

Titanium tetraisopropoxide (97%) was procured from Aldrich, USA. Nitrobenzene (NB) AR grade (99.0%), methylene blue (MB) and malachite green (MB) were procured from S.D. Fine Chem. Limited, India. Acetophenone (AP) AR grade and chemical oxygen demand (COD) standard chemical reagents (solution A: 1.14538; solution B: 1.14681 and 1.14682) were purchased from E. Merck, India. The molecular structure and chemical properties of these substances are given in Table 1.

2.2. Synthesis of catalysts

Nanocrystalline TiO₂ of anatase and rutile phase was synthesized by hydrolysis of titanium tetraisopropoxide. The mixture of dry ethanol (100 ml) and titanium tetraisopropoxide (30 ml) was taken in a 250 ml round bottom flask and continuously stirred for 30 min, followed by ultrasonication for 30 min. Hydrolysis of titanium tetraisopropoxide solution was carried out by adding distilled water (24 ml) slowly at the rate of 0.5 ml/min with continuous stirring. The solvent from the obtained mixture was removed using rotavapour (Buchi, R-205) at 343 K under reduced pressure. The powder was then kept in an oven at 393 K overnight. The dried sample was calcined at different temperatures of 753 and 1023 K under air for 11 h, and the calcined samples are termed as AT (anatase TiO₂) and RT (rutile TiO₂). Calcination of AT was carried out in a tubular furnace under airflow (flow rate = 3 L/min) up to 913 K. Sample RT was calcined in a muffle furnace without airflow.

2.3. Catalyst characterization

Powder XRD patterns were recorded with a Phillips X'pert MPD system using CuK α radiation ($\lambda = 0.15405$ nm) in a 2θ range of 5–60° at a scan speed of 0.1° s⁻¹. XRD patterns were compared with the standard anatase and rutile

Table 1			
Molecular structure and	chemical	properties	of substrates

(a) Acetophenone (AP)	Molecular weight	120.15		
\sim	Chemical formula	C ₈ H ₈ O		
/	Absorption maximum	244 nm		
	Color	Colorless		
(b) Nitrobenzene (NB)	Molecular weight (amu)	123.11		
	Chemical formula	C ₆ H ₅ NO ₂		
°	Absorption maximum	268 nm		
	Color	Colorless to pale yellow		
(c) Methylene blue	Molecular weight (amu)	319.86		
(H ₃ C) ₂ N	Chemical formula	C ₁₆ H ₁₈ ClN ₃ S		
Cl	Solubility in water	3.55%		
	Absorption maximum	644 nm		
	Class	Thiazin		
(d) Malachite green	Molecular weight (amu)	927.02		
N(CH ₃) ₂	Chemical formula	$C_{52}H_{54}N_4O_{12}$		
C = √ → (CH ₃) ₂				
	Solubility in water Absorption maximum	Very soluble 628 nm		
	Class	I riarylmethane		

diffractograms [10]. The phase percentage formed was determined from the integrated intensity at $2\theta = 25.3^{\circ}$ (101) for anatase and the peak at $2\theta = 27.4^{\circ}$ (110) for rutile. The percentage of anatase, A (%), was determined as follows [11]:

$$A(\%) = \frac{100}{1 + 1.265(I_{\rm R}/I_{\rm A})},\tag{1}$$

where $I_{\rm R}$ is the intensity of the rutile peak at $2\theta = 27.4^{\circ}$ and $I_{\rm A}$ is the intensity of the anatase peak at $2\theta = 25.3^{\circ}$. Crystallite sizes of samples were calculated from the half-height width of different peaks of anatase using the Scherrer equation. Characteristic peaks of $2\theta = 25.3^{\circ}$ (101) for anatase and $2\theta = 27.4^{\circ}$ (110) for rutile using the Scherrer formula with a shape factor K of 0.9 [12] were

used. Crystallite size, Cs, was determined as follows:

$$Cs = \frac{K\lambda}{W\cos\theta},\tag{2}$$

where $W = W_{\rm b} - W_{\rm s}$; $W_{\rm b}$ is the broadened profile width of experimental sample and $W_{\rm s}$ the standard profile width of reference sample, λ is the wavelength of X-ray radiation (CuK $\alpha = 0.15405$ nm) and θ is the diffracting angle. Highpurity silicon was used as an internal standard to account for the instrumental line-broadening effect during crystal size estimation.

Specific surface area, pore volume and pore size distributions of calcined samples were determined from N_2 adsorption–desorption isotherms at 77 K (ASAP 2010, Micromeritics, USA). Surface area and pore size distribution were determined using the BET equation and BJH method, respectively [13]. The samples were degassed at 623 K under vacuum (10⁻³ Torr) for 4 h, prior to measurement.

The band-gap energy of the nanocrystalline TiO_2 was determined using DRS (Shimadzu UV-3101PC) equipped with an integrating sphere and $BaSO_4$ was used as a reference [14–16]. The spectra were recorded at room temperature in the wavelength range of 250–600 nm. The band-gap energy of anatase and rutile TiO_2 was determined using the DR–UV—visible (vis) method and calculated according to the equation for band-gap energy EG (eV):

$$EG = hc/\lambda,$$
(3)

where *h* is Planck's constant, *c* the light velocity (m/s) and λ the wavelength (nm).

An FT-IR spectrophotometer (SPECTRUM GX, Perkin-Elmer) was used to determine the specific functional groups in TiO₂ samples. The sample was kept at 100 °C for 2 h under vacuum before FT-IR analysis.

A scanning electron microscope (Leo series 1430 VP) equipped with INCA was used to determine the morphology of samples. The sample powder was supported on aluminum stubs using silver paint and then coated with gold by plasma prior to measurement.

2.4. Photocatalytic irradiation system

The photocatalytic activity of anatase and rutile phases in amorphous and nanocrystalline form was determined by studying the decomposition of aqueous solutions of substances in a photocatalytic reactor. The concentration of the substance was taken as 50 ppm in water. The photocatalytic reactor consists of two parts. The first part is the inner quartz double-wall jacket with an inlet and outlet for water circulation to maintain the temperature of the reaction mixture. This jacket has an empty chamber at the center for immersion of a 125 W mercury vapor lamp (Crompton, high-pressure mercury vapor lamp, with the glass bulb removed, radiation wavelength 200–500 nm) used for irradiation of the reaction mixture. The second part is the outer borosilicate glass container (volume 250 ml after insertion of the inner part) in which the aqueous solution is taken and irradiated. It was cooled by water circulation to room temperature during the experiments. The concentration of substance in bulk solution prior to irradiation was used as the initial value for the measurement of degradation of the substance. At each interval of 1 h, 5 ml of sample was withdrawn by a syringe from the irradiated suspension. The catalyst was separated by centrifugation from the aqueous solution prior to analysis. Before commencing irradiation, a suspension containing 50 mg of the catalyst and 250 ml aqueous solution of about 50 ppm of substance was ultrasonicated for 2 min and then stirred for 30 min in the dark, and to determine the adsorption on catalyst, 10 ml of sample was withdrawn by syringe for analysis. A blank study was also carried out only in the presence of UV light without any catalyst. It shows that even though there is a large decrease in UV/vis absorbance, the COD values are well decreased only in the presence of the TiO₂ catalyst. This shows that though during UV irradiation, direct photolysis of dyes could occur, mineralization of dyes only takes place in the presence of a photocatalyst.

2.5. Chemical analysis

The UV–vis absorbance of aqueous solution of substrate was measured by a UV–vis spectrophotometer (Cary 500, Varian) at their respective λ_{max} (Table 1) equipped with a quartz cell having a path length of 1 cm. The spectral absorbance was measured with baseline correction with a scan rate of 600 nm min⁻¹ and a data point interval of 1 nm. The concentration of substrates in the solution was determined by using the calibration curve of respective substances (concentration vs. absorbance) prepared with their known concentrations.

The oxygen equivalent of the organic matter of a sample, i.e., COD, was measured by using a SPECTROQUANT[®] NOVA 60 photometer. The reagents for COD analysis and 3 ml of sample taken at different times were mixed together in glass cells and digested in a Spectroquant TR 320 thermodigester for 2 h at 148 °C. After digestion, the mixture was cooled to room temperature and COD was measured using the photometer for the original solution and the centrifuged sample that was taken out at different time intervals.

3. Results and discussion

3.1. Crystallinity and crystallite size

The XRD patterns of nanocrystalline anatase and rutile TiO_2 samples are shown in Fig. 1. The pattern shows that the catalyst calcined at 753 K has 100% anatase phase and the one calcined at 1023 K has 100% rutile phase, and both are highly crystalline in nature. The crystallite sizes for the anatase and rutile samples were calculated to be 14 and 32 nm, respectively. It is well known that the crystal phase



Fig. 1. XRD pattern of anatase and rutile nanocrystalline TiO2.

transformation from anatase to rutile phase occurs on calcination of TiO_2 powder at a temperature higher than 753 K [17].

3.2. FT-IR spectroscopy

Fig. 2 shows the IR transmission spectra of anatase and rutile nanocrystalline powder [18]. The broad bands at 3401 and 1630 cm^{-1} observed in anatase nanocrystalline TiO₂ spectra are assigned to the Ti-OH stretching modes [17–19]. In the anatase sample, the spectrum shows the intensive band of OH-group stretching at $3200-3550 \text{ cm}^{-1}$ (O–H asymmetrical and symmetrical stretching vibrations) and deformation vibration at $1600-1630 \text{ cm}^{-1}$ (H–O–H), which is evidence for the large amount of water molecules [19]. In the rutile sample, the fact that the Ti–OH vibration band becomes much weaker and the complete removal of the absorption peak at 1630 cm^{-1} indicates the absence of hydroxyl groups in rutile nanocrystalline TiO₂.

3.3. Textural properties

It was observed that anatase nanocrystalline TiO₂ has a surface area of $124 \text{ m}^2 \text{ g}^{-1}$, with 7.5 nm average pore diameter, whereas for the rutile nanocrystalline TiO₂ the surface area was observed to be $2 \text{ m}^2 \text{ g}^{-1}$, with pore diameter 5.4 nm. This is attributed to the fact that during calcination, good crystalline phases develop, resulting in denser packing of particles and reduction of porosity of samples. The decrease in the surface area of rutile TiO₂ is due to the sintering. N₂ adsorption isotherms for AT and



Fig. 2. FT-IR spectra of anatase and rutile nanocrystalline TiO2.



Fig. 3. $N_{\rm 2}$ adsorption isotherms of anatase and rutile nanocrystalline TiO_2.

RT are shown in Fig. 3. N_2 adsorption isotherms measured at 77 K were of type IV typically observed for anatase TiO₂ showing mesoporosity, and for rutile TiO₂ were of type III reflecting marginal porosity. The pore size distribution of anatase and rutile TiO₂ is shown in Fig. 4.

3.4. Electronic properties

DRS spectra of nanocrystalline TiO_2 samples are shown in Fig. 5. To obtain a more precise band edge for these semiconductor powders, a differential calculation was done and the resulting curves are shown in Fig. 5 (inset). The band edges of the samples determined from differentiation of anatase and rutile were 400 and 411.9 nm, respectively, which correspond to band-gaps 3.1 and 3.0 eV for anatase and rutile TiO₂, respectively.

The crystallite size of anatase nanocrystalline TiO_2 increases with respect to calcination temperature with decrease in band-gap values. The smaller band-gap values are indicative of relatively densely packed crystalline structures. This is supported by surface area and pore volume data obtained for anatase and rutile nanocrystalline TiO_2 . It is well known that the band-gap of a



Fig. 4. Pore size distribution of anatase and rutile nanocrystalline TiO₂.



Fig. 5. DRS spectra of anatase and rutile nanocrystalline TiO_2 (inset: differential spectra of DRS).

semiconductor decreases with increase in crystallite size of TiO_2 .

3.5. Morphology

Micrographs of the TiO_2 samples given in Fig. 6 show globular morphology of the particles. Sintering of the particles is clearly observed with increasing calcination temperature.

3.6. Photocatalytic activity

The photocatalytic activity of both anatase and rutile TiO₂ particles was investigated using degradation of aqueous NB, AP, MB and MG solutions. The adsorption of substances was determined after 30 min of stirring the mixture of substance solution and catalyst. The percentage of adsorption using AT catalysts was found to be 9%, 8%, 24% and 28% and using RT catalysts 2%, 2%, 10% and 12% for substances AP, NB, MB and MG, respectively. These results confirm that the adsorption of substances on the surface of AT was higher due to the higher surface area and mesoporosity. The spectra recorded after illumination of UV light with respect to time are shown in Fig. 7 using anatase nanocrystalline TiO₂. There was no additional peak observed during the photocatalytic degradation of AP and NB, while in the case of MB two peaks were initially observed at 663 and 612 nm, which merged and the maximum absorbance was finally observed at around 636 nm; for MG, peaks observed at 426 and 316 nm shifted to 365 and 250 nm with initially higher absorbance and become reduced with the irradiation of UV light.

Fig. 8 shows the photocatalytic activity of anatase nanocrystalline TiO₂. It can be seen from the figure that the degradation of dyes (MB and MG) is faster as compared to organic compounds (AP and NB) in the case of anatase as well as rutile TiO₂. The complete degradation of dyes took place within 1 h, while in the case of NB and AP it was observed 80% and 100%, respectively, in 4 h of irradiation with ultraviolet light.

Fig. 9 shows that the degradation of substances is slower with the rutile sample compared to the anatase sample.



Anatase TiO₂

Rutile TiO₂

Fig. 6. SEM images of anatase and rutile nanocrystalline TiO₂.



Fig. 7. UV-visible absorption spectra of (a) AP, (b) NB, (c) MB and (d) MG with respect to irradiation time using anatase nanocrystalline TiO_2 . (a) Two times diluted and (b) and (c) four times diluted.



Fig. 8. Degradation of different substrates using anatase nanocrystalline ${\rm TiO}_2$.

The degradation of MG was 100% in 3 h, while the degradation of MB, AP and NB was observed to be 85%, 92% and 52%, respectively, in 4 h of irradiation time. This clearly indicates that the photocatalytic activity of anatase is higher than rutile nanocrystalline TiO_2 and also that it varies with the nature of the substances.

The better photocatalytic activity of the anatase TiO_2 may be due to (a) surface area and porosity, (b) hydroxyl group and



Fig. 9. Degradation of different substrates using rutile nanocrystalline TiO_2 .

(c) band-gap. It is obvious that the higher surface area with larger pores plays an active role in the adsorption of substance, which results in the higher photocatalytic activity. The higher surface area also provides a higher number of catalytic sites on the surface of TiO_2 with less recombination of electron hole pairs, which is the rate-determining step in the photocatalytic degradation. The FT-IR spectra showed that the hydroxyl groups are higher in the case of anatase as compared with

rutile TiO₂. The photocatalytic process is highly dependent on the hydroxyl group present on the surface, which attacks the contaminant present in water. The higher surface area is helpful in accommodating higher hydroxyl groups, which leads to higher photocatalytic degradation. The optimum band-gap also plays a major role in the photocatalytic activity of anatase TiO₂. Electron hole pair generation is dependent on the bandgap of TiO₂; the increase in the band-gap is useful in obtaining higher electron hole pair generation. The results show that the hydroxyl (OH) groups present in anatase are higher as compared with rutile nanocrystalline TiO₂, which are beneficial for the photocatalytic activity.

The initial rate of degradation of substance determined for both catalysts is given in Fig. 10, which clearly shows higher photocatalytic activity of anatase than that of rutile nanocrystalline TiO_2 using UV source having spectral distribution shown in Fig. 11.



Fig. 10. Initial rate of degradation of different substrates using anatase and rutile nanocrystalline TiO₂.



Fig. 11. Spectral distribution of the UV source.

Table 2

Decrease in COD value of different substrates using anatase and rutile nanocrystalline ${\rm TiO}_2$

COD of reaction mixture of dyes w.r.t. irradiation time (mg/L)										
Substrates	Catalysts									
	Anatase (AT)			Rutile (RT)						
	1 h	2 h	3 h	4 h	1 h	2 h	3 h	4 h		
AP NB MB MG	22 31 08 12	18 25 00 00	15 20 00 00	10 15 00 00	36 52 22 20	29 50 16 16	25 46 12 10	21 43 08 04		

Initial COD of AP = 120 mg/L; NB = 90 mg/L; MB = 65 mg/L; MG = 75 mg/L.

The decreases in COD values are given in Table 2 for different substances using anatase and rutile nanocrystalline TiO₂. These results confirm the complete mineralization of MB and MB dyes and partial mineralization of organic compounds AP and NB using anatase nanocrystalline TiO₂. The COD values could not reach zero in the case of organic compounds for both anatase and rutile nanocrystalline TiO₂. The COD values of rutile for all substances are higher as compared with anatase, which also confirms the lower photocatalytic activity of rutile TiO₂.

4. Conclusion

Anatase and rutile nanocrystalline TiO₂ have been prepared by hydrolysis of titanium tetraisopropoxide and characterized by different physical techniques. The crystallite sizes of anatase (14 nm) and rutile (32 nm) nanocrystalline TiO₂ are changed because of thermal treatment. Anatase nanocrystalline TiO₂ was mesoporous with $124 \text{ m}^2 \text{g}^{-1}$ surface area. There was a shift in the absorption edge of 11.9 nm observed in rutile, which leads to lower band-gap than anatase nanocrystalline TiO₂ due to increase in particle size. The catalysts have been tested for the photocatalytic degradation of AP, NB, MB and MG, which are found in different industries' effluents. Higher photocatalytic activity of anatase nanocrystalline TiO₂ was obtained as compared with rutile TiO₂. Studying the reason for the higher photocatalytic activity of the nanocrystalline TiO₂ catalysts is still under progress.

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