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SYNTHESIS AND CHARACTERIZATION OF TiO_2NANOCRYSTALS BY SOL-GEL METHOD AND TO STUDY THE EFFECT OF CALCINATION TIME ON THE ITS PHOTOCATALYTIC ACTIVITY

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ABSTRACT
TiO_2 nanoparticles were prepared by a simple sol-gel method at different calcinations time. The prepared samples were characterized by X-ray diffraction and UV visible spectroscopytechniques. The formation of hydroxyl radicals (•OH) on the surface of UV light illuminated TiO_2 nanoparticles was detected by UV visible absorption spectroscopic technique. The photocatalytic activity was evaluated by photocatalyticdecolorization of Methelene Blue (MB) aqueous solution under UV light irradiation. The results revealed that the TiO_2 could be crystallized via sol-gel method. The light absorption, the formation rate of hydroxyl radicals, and photocatalyticdecolorization of MB aqueous solution were significantly enhanced for mixed phase instead of simple anatase or rutile phase.

Keywords: *TiO_2, photocatalytic, degradation, sol-gel, calcination.*

I. INTRODUCTION
Semiconductors having band gap energies adequate for endorsing and catalyzing a broad range of chemical reactions are of environmental importance [1]. Among many semiconductors, TiO_2 has established to be the most suitable for prevalent environmental applications because of its biological and chemical unresponsiveness, constancy against photo corrosion and chemical corrosion, and cost-efficiency [2-5]. Most important is its photocatalytic property which enables its application for the purification of water, self-consciousness of growth of unwanted microbes and self cleaning surfaces [6,7]. The photocatalytic process involves the degradation of the organic pollutant when TiO_2 is irradiated with Ultra Violet (UV) light in presence of the aqueous solution of the organic pollutant. Fujishima and Honda in 1972 reported thephotocatalytic activity of TiO_2 for the first time. Since then, there has been a greatresearch going on in this field. To boost the photocatalytic activity of TiO_2, several methods have been discovered. The photocatalytic efficiency of TiO_2 particles largely depend upon their microstructure,crystalline structure, particle size as well as on the impurities present. Because ofthese factors the preparation conditions have large influence on its photocatalytic efficiency.Nanostructures of TiO_2 are investigated on a large scale as they posses high specific surfacearea which is used up for degradation. The role of different crystalline phases of TiO_2, mainly
anatase and rutile phase has also been extensively studied in respect of TiO_2/UV process.Anatase phase is found to be showing highest photocatalytic activity. However, the composition of different phases, are reported to show better photocatalytic degradation. Degussa P25, is commercially obtainable, shows very good photocatalytic degradationconsists of two forms of TiO_2 (approximatly1:3 ratio of rutile :anatase). Theproposed mechanism based on generation of electron-hole couples with strong redoxproperties has been used as a platform to explain the differences in the photocatalyticefficiencies observed in these systems [8]. Extensive work has also been carried out in orderto improve the photocatalytic efficiency of nanoparticles of TiO2 by using differenttechniques like doping and using support catalyst. Support catalyst such as graphite [9,10],carbon nanotubes(Yao) and activated carbon [11,12]. Doping lead to the formation ofinterstitial sites which act as trapping sites and thus, increase the recombination time. Thisincreases the possibility of redox reactions. Support catalyst has impact on the growthphenomenon and hence it controls various phase formations. It forms junction with TiO_2 andhence controls the flow of charge carriers.
In this paper TiO_2 powder was synthesized by sol-gel method. The sol formed wascalcined at different time. Different phase formation andcrystallite size was observed. The activity of TiO_2 was studied by observing photocatalyticdegradation of methylene blue (MB) under UV light. Calcination time was optimized by observing photocatalytic degradation of methylene blue (MB). Several batchesof synthesis were carried on. Thework is important as here we got positive results for particular time. Also, the change incrystalline nature is vital, as it can be used to control the phase of TiO_2. This paper includes the theoretical back ground of the work, the

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experimentaltechniques involved in the work and the detailed results of the experiment. The conclusionsare discussed in detail on the basis of theory and observed results.

II. EXPERIMENTAL

TiO_2 was synthesized using Sol-Gel method using titanium alkoxide as a startingmaterial. Titanium alkoxide in isopropyl alcohol form sol through the process of thehydrolysis i.e. the small particle of hydroxide of titanium get dispersed in the solution to formsol. This sol when further reacted undergoes gelation giving nanocrystalline porous gel. Thenanocrystalline porous gel is heated to convert it into crystallites. Titanium dioxide (TiO_2) powder was prepared by a Sol-Gel (SGS) thchniqe.

Chemicals: Titanium tetra isopropoxide [$(Ti(OCH(CH_3)_2)_4$] (Spectrometer Pvt. Ltd. Mumbai, Mol. Wt. 284.25), Isopropyl alcohol [$(CH_3)_2CHOH$] (Thomas Baker, Mol. Wt. 60.10), Nitric acid [HNO_3](Thomas Baker, Mol.Wt. 63.01) and Double Distilled water [H_2O].

We have taken the weight ratio of [$(Ti(OCH(CH_3)_2)_4$] : $(CH_3)_2CHOH$: H_2O : HNO_3 asis 1:10:1:0.2 for the formation of SGS in order to synthesize TiO_2. 40ml isopropyl alcohol(IPA) was taken in a beaker and titanium tetra isopropoxide (TTIP) was added dropwise in itwhich act as a precursor of TiO_2 in this reaction. During the addition of TTIP to IPAcontinuous stirring is required. After 30 minutes of stirring at room temperature, solution iskept at constant temperature of 80^OC. 0.8 ml of 10% HNO_3 and 4 ml distilled water is thenadded drop wise with continuous stirring. After addition of water, solution forms gel structure. This gel like structure is due to formation of $Ti(OH)_4$ linkage as shown in the reaction below. This gel was stirred at 80^OC till it sufficiently dried to become paste. This paste was kept in furnace (Indfurthyristorised furnace, 4.5 kWs) for calcination to get nanocrystallineTiO_2.We have synthesized TiO_2 for different calcination temperatures (250OC to 750OC instep of 100OC) at constant calcination period. Six samples were prepared which weresubjected to photocatalytic degradation. The calcination temperature at which maximumdegradation was kept constant for further synthesis. The samples obtained were, then used to observe photocatalyticdegradation. The calcination temperature was optimized, based on photocatalytic activity.

$$Ti((CH_3)_2CHO)_4 + (CH_3)_2CHOH + H_2O \xrightarrow{HNO_3} Ti(OH)_4 + 5(CH_3)_2CHOH \uparrow$$

$$Ti(OH)_4 \xrightarrow{Heat} TiO_2 + 2H_2O$$

III. RESULTS

X-ray Diffraction:

As synthesized samples of TiO_2, were characterized by XRD, to study the detailed crystalline nature of particles and their phase formation. The XRD measurements were performed on a X-ray diffractometer using Cu Kα irradiation (λ=0.154nm). Data were recordrd for a range of 20º to 80º with a step width of 0.1º. We have investigated the structural transformations of a mixed anatase-rutile nanocrystalline TiO_2 nano particles in effect of the annealing temperature. The determination of TiO_2 phase and the crystallite size upon isochronal and isothermal calcination the powder in air at temperatures ranging from 250ºC to 750ºCK in steps of 100ºC was done by XRD technique. We can calculate percentage of phases in the sample. In order to quantify that XRD peak intensity ratios were used. The ratio between anatase and rutile extracted from XRD spectra was computed with the empirical relationship [10].

$$R(T) = 0.679\left(\frac{I_R}{I_R + I_A}\right) + 0.312\left(\frac{I_R}{I_R + I_A}\right)^2$$

where,

$R(T)$ is the percentage content of rutile at each temperature,
$I_A$is the intensity of the main anatase reflection (101) (2θ =25.30°), and
$I_R$is the intensity of the main rutile reflection (110) (2θ =27.44°).

The X-ray diffraction pattern of TiO_2calcined at different temperatures is shown inFigure1. The lower two curves show the X-ray diffraction peaks of anatase and rutilephases of TiO_2 as reported in the X-ray diffraction data files (JCPDS). Remaining graphs are the X-raydiffraction graphs of as synthesized samples with decreasing calcination temperatures as wesee from lower graph to upper graph as indicated in the Figure 1. From Figure 1, it isobserved that for lower calcination temperatures the X-Ray diffraction peaks have larger fullwidth half maximum indicating

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lesser crystalline nature. As calcination temperature increases,peaks become narrow, as a result of increased crystalline nature. This is also evident from thecrystallite size calculations by Sherrer formula shown in Table 1. With increase incalcination temperature, the crystallite size increases. It can also be seen that at lowertemperature, percentage of anatase phase, which is a metastable state, is higher whilepercentage of rutile phase is lower. As temperature increases, percentage of anatase decreasesand percentage of rutile increases.

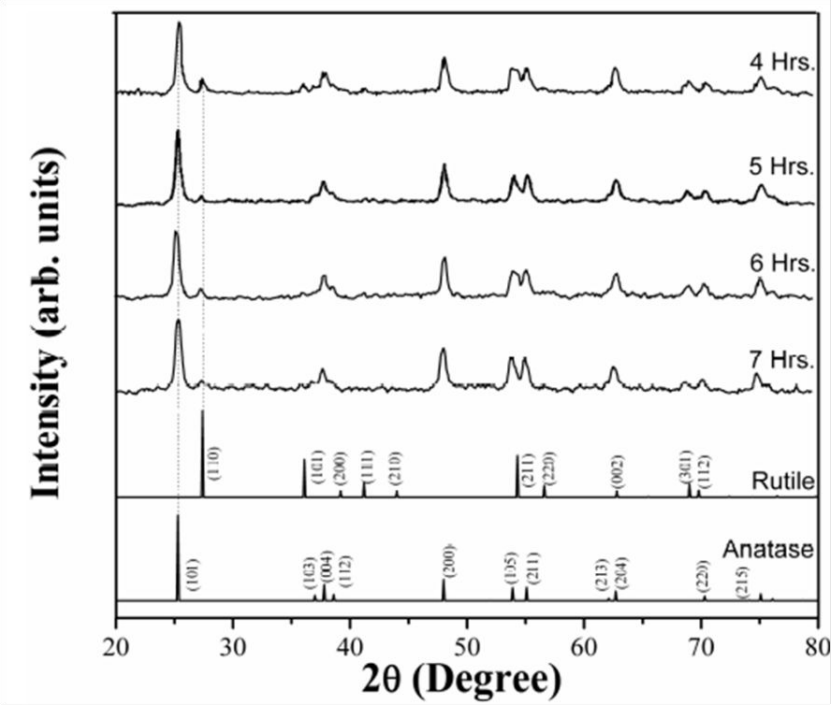

Figure 1: X-ray diffraction pattern of as synthesized samples of TiO_2 at differentcalcination time.

UV-Visible absorption:
UV-Visible absorption spectroscopy was used for determining the band structure of the as synthesized samples. Also, it was used to observe the photocatalytic degradation.Figure 2 shows the UV-Visible absorption spectra of as synthesized TiO_2 samplescalcined at different temperatures. It can be observed from the graph that as the calcinations temperature is increased the defect states decrease. This is also in accordance to XRDanalysis. With increase in calcination temperature the crystallinity increases, thus theamorphous nature decreases and hence the defect states decrease. The sharp fall in absorbanceis maximum for the sample calcined at 750°C and the band gap is found to be 2.96 eV. Theband gap values as observed from the graph are written in Table 1.

Degradation:
Figure 3 shows the UV-Visible absorption graph of MB. Theabsorption of MB is maximum at wavelength 664 nm. As the concentration of MB isdecreased the absorption also decreases. Hence, relative change in concentration of MB canbe observed by absorption measurements. Here, the pink curve corresponds to the absorptioncurve of 10-**5**M solution of MB. The other curves correspond to the absorption curves of MBsame solution treated with TiO_2 particle under UV light exposure for 30 min. It was observedthat the maximum degradation (means minimum absorption) was shown by TiO_2calcined at 550°C.

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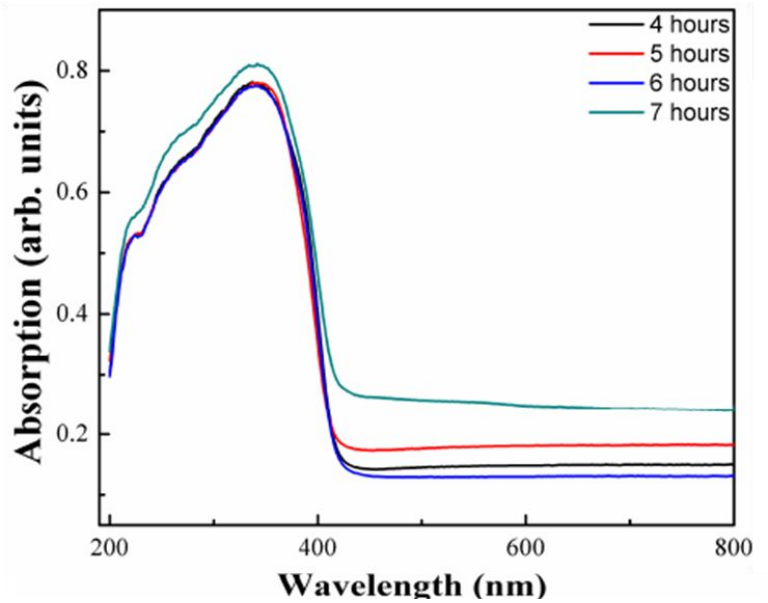

Figure 2: UV-Visible absorption spectra ofas synthesized TiO_2 samples calcined at different time.

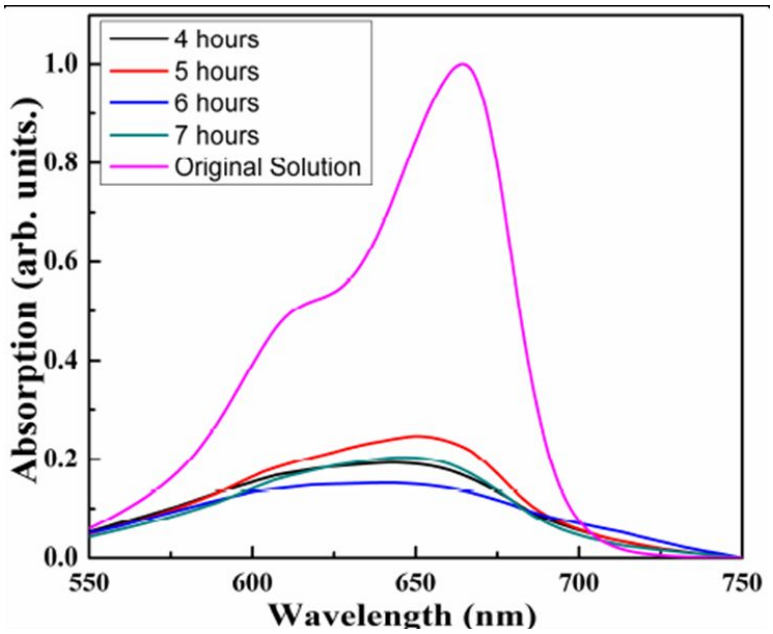

Figure 3: UV-Visible Absorption graph of MB after degradation using as synthesized TiO_2 samples calcined at differenttime.

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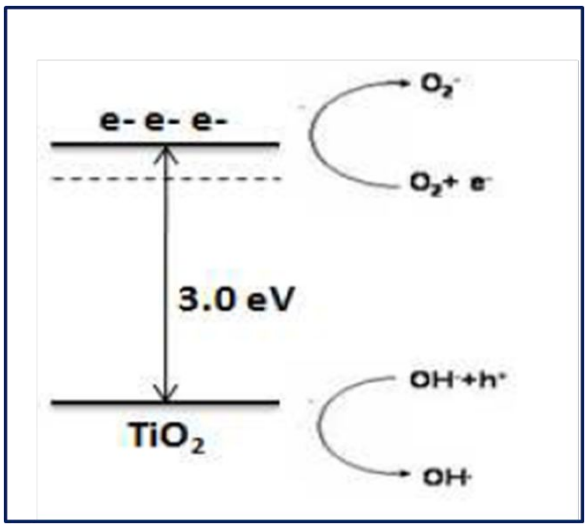

Figure 4: Redox reactions that take place at the surface of (bulk) TiO_2.

IV. DISCUSSIONS

Photocatalysis over a semiconductor oxide such as TiO_2 is initiated by the absorptionof a photon with energy equal to or greater than the band gap of the semiconductor, producing electron-hole (e^-/h^+) pairs.Consequently, following irradiation, the TiO_2 particles can act as either an electrondonor or acceptor for molecules in the surrounding medium. The electron and hole canrecombine, releasing the absorbed light energy as heat, with no chemical effect. Otherwise,the charges can move to "trap" sites at slightly lower energies. The charges can still
recombine, or they participate in redox reactions with adsorbed species. A simplifiedmechanism for the photo-activation of a semiconductor catalyst is presented in figure 4. The valence band hole is strongly oxidizing, and the conduction band electron isstrongly reducing. At the external surface, the excited electron and the hole can take part inredox reactions with adsorbed species such as water, hydroxide ion (OH^-), organiccompounds, or oxygen. The charges can react directly with adsorbed pollutants, but reactionswith water are far more likely since the water molecules are far more populous thancontaminant molecules.
There are two routes through which OH radicals can be formed. The reaction of theValence-band "holes" (h^+_{vb}) with either adsorbed H_2O or with the surface OH^- groups on theTiO_2 particle. H_2O will adsorb and react with a hole in the valence-band and an acceptor (A)such as dioxygen will also be adsorbed and react with the electron in the conduction band(e^-_{cb}). Oxygen can trap conduction-band electrons to form superoxide ion ($O^{2\bullet-}$). Thesesuperoxide ions can react with hydrogen ions (formed by water splitting), forming $HO^{2\bullet}$. Acompetition reaction occurs between water, oxygen, organic molecules and trace metalswhich may be present in the system. Oxygen molecules will be reduced and give activespecies ($O^{2\bullet-}$). Water will be oxidized by the hole in the valance band to give the very activefree radical •OH which can oxidize organic species.

Table:

Table 1.Details of as synthesized samples of TiO_2 at different calcinations time.

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Sr. No.	Calcination Time (Hrs)	Anatase (%)	Rutile (%)	A/R ratio	Crystallite size (nm)	BandGap (eV)
Error	-		±1%		±0.5 nm	±0.1 eV
1	4	90	10	9.00	35.39	3.03
2	5	88	12	7.33	32.56	3.04
3	6	87	13	6.69	29.07	3.05
4	7	85	15	5.67	27.13	3.08

V. CONCLUSION

TiO_2 nanoparticles can be facilely prepared by asimple sol-gel method at different calcination timeand assisted with photodegradationtechnique. Results shows as the calcination timeto some extent increases crystallanity, size and band gap remains almost comparable. Moreover, degradation is higher for 6 hours calcinations time. The finding of this work is, the aborption of light, the hydroxyl radicals formation rates, and photocatalyticdegradation of MB aqueous solution were significantlydependanton particular percentage of anatase to rutile ratio. Only anatase or rutile phase shows less degradation rate as compare to mixed phase.

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