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Cr-Doped Tio_2: Synthesis and Photodegradation of Methylene Blue Dye

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Abstract
Cr-doped TiO_2 photocatalyst were synthesized successfully by aEDTA-Glycol method. Ethylenediamine was used as a source of N dopantsto extend and improve the photoresponse of the materials to UV light. The photocatalysts werecharacterized by several techniques to determine the structural, textural and optical characteristics.The activity of the materials was tested in the photodegradation of methylene blue (MB) dye. Factors affecting the photodegradation process were studied.

Keywords: *TiO2; Cr-doped TiO2; Photocatalysis; N-doped TiO2; Methylene Blue Dye;*

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I. Introduction

TiO_2 based semiconductor materials have been widely studied for environmental applications due to their efficiency on the degradation and mineralization of organic pollutants in water [1-4]. TiO_2 shows non-toxicity, low cost, chemical stability, resistance to corrosion, and high reactivity under ultraviolet light (λ<387 nm). Recently many researchers have explored different methods to improve visible-light response of TiO_2, such as dye sensitization, fabrication of a heterojunction with another semiconductor and doping with nonmetal (N, B, F, etc.) and metal elements (Sn, V, Cr, etc.) [5-18].Among all these, the introduction of metal dopants (especially transition metal) into the TiO_2 lattice is a simple and effective means. As one of the transition metals, Cr has been widely used as the dopant since Cr doping can narrow the band gap and extend the photoresponse to the visible-light range [19–22]. The incorporation of metal dopant ions into the crystal lattice of semiconductor TiO_2 has been widely studied. The transition metal ion dopants expand the light absorption from UV to the visible region, leading to the improvement of the photo-response of TiO_2 by introducing additional energy levels within the band gap of TiO_2 by the dispersion of the metal ions in the TiO_2 matrix [23, 24]. Furthermore, transition metal dopants inhibit electron-hole recombination during irradiation by increasing the charge separation and therefore the efficiency of the photocatalytic process.

Chromium(III) ion (Cr^{3+}) has been considered an appropriate dopant candidate, because the similar ionic radius of Cr^{3+} (0.63 nm) compared to that of Ti^{4+} (0.68 nm) enables the easy incorporation of chromium into the crystal lattice of TiO_2 [25-27]. Moreover, the Cr-doped samples may even exhibit inferior UV-light photocatalytic activity compared to TiO_2. In fact, the enhancement of the photocatalytic activity under visible light irradiation has been demonstrated by doping TiO_2 with Cr^{3+} ion, with the consequent retarding of the recombination process of electron-hole pairs [26].

The material properties of the prepared catalyst seem to be strictly dependent on the crystal structure of the catalyst, the size and morphology of the nanoparticle, which are correlated with the method of synthesis, and the dopant content. Furthermore, the preparation techniques used to synthesize transition metal doped TiO_2 materials play animportantroleonthephotostabilityofthecatalystbecausethesedopantsgenerallyexhibit different oxidation states and therefore redox reactions could take place during the synthesis [27].

On the above grounds Cr^{3+}-doped titanium dioxide was prepared by EDTA-Glycol method. The prepared catalyst was characterized by X-ray diffraction (XRD), ultraviolet–visible diffuse reflectance spectroscopy (UV–Vis DRS), N_2 adsorption–desorption analysis, scanning electron microscopy (SEM), transmission electron microscopy (TEM) and photoluminescence (PL) spectroscopy.For photocatalytic evaluation activity, methylene blue indicator (MB) was chosen as a model pollutant.The photocatalytic activity of the Cr^{3+}-doped TiO_2 was assessed by degradation of MB aqueous solution under UV light and was subsequently compared with the performances of the pure TiO_2 and Degussa P25. Moreover, the stability and recyclability of the Cr^{3+}-doped TiO_2 catalyst for MB degradation wasevaluated.

II. Experimental

2.1 Synthesis of Undoped and Cr doped TiO$_2$

All chemicals were obtained from the indicated sources and used without further purification.Titanium tetraisopropoxide (TTIP, 98% Sigma Aldrich), Chromium nitrate (98% Sigma Aldrich), Ethylene diamine tetra acetic acid (EDTA, 98% Sigma Aldrich), Iso propanol (99.9% Sigma Aldrich), Ethanol (99.9%Sigma Aldrich) and distilled water (DW).

The solution of Titanium isopropoxide (TTIP) prepared in ethanol-Iso propanol (1:1). To this solution, calculated amount of chromium nitrate (CN) was added to get the materials with the atomic ratio of Cr to Ti in the precursor as 1%, 4%and 7% respectively. To this mixture, different amounts of EDTA and EG were added under the stirring condition. The prepared mixtures were then continuously stirred for 4 h to obtain a gel like material. After 4 hstirring, they were transferred into auto-clavesandheatedat200˚Cfor5h.Theprecipitateswererinsed with ethanol and were collected by centrifugal separation. Pure and doped TiO_2nanomaterials were finally obtained by calcinationof the precipitates at 450˚C for 2hat the heating rate of 10°C/min.

Table 1 Atomic ratio, Crystalline Phase, Lattice parameters and Average Crystallite Size of prepared samples.

Sample Code	Atomic Ratio of Cr (%)	Crystalline Phase	Crystallite Size (nm)	Lattice Parameters (Å)	
				a = b	c
TiO_2	0	Anatase	19.8	3.783	9.523
TC-1	1	Anatase	18.9	3.784	9.523
TC-4	4	Anatase	10.8	3.784	9.523
TC-7	7	Anatase	21.6	3.787	9.526

2.2 Characterization

Crystallographic phase analysis was carried out from powder X-ray diffraction (XRD)measurements using a Phillips analytical diffractometer with Ni-filtered Cu Kα radiation. Theaverage crystallite size of anatase and rutile phases was determined from the Scherer equationafter correcting for the instrumental broadening. TEM (Transmission electron microscope) data were obtained usinga 200 kV FEI Tecnai T20 machine.EDS (Energy dispersive X-ray) spectroscopy was used to determine theapproximate elemental composition of the samples.BET surface area, porevolume, and pore size distribution profiles were obtained using a Micromeritics ASAP 2020analyzer. About 100 mg of a sample was degassed under vacuum (10^{-6} Torr) at 300°C, prior toN_2 adsorption. The BJH method was employed to obtain the pore size distribution.UV–vis absorptionandPLspectrameasurementswerecarried out usingportablemultichannelopticalspectrumanalyzer.

2.3 Photocatalytic Decolorization of Methylene Blue (MB)

The photocatalytic reactivity of N-doped TiO_2 was evaluated by the decolorization of MB under visible light irradiation (> 400 nm). A LED lamp of 15 W was used as a light source for testing. Different amounts of the Zn-doped TiO_2 powder was added into 20 ml of 5-20 mg/L MB solution. Before open LED light, the suspension was put in the reactor and stirred until dye adsorption was completed. After that, the LED light was turned on. The concentration of MB dye solution was evaluated at given time intervals of every 30 min by using UV-vis spectrophotometry at wavelength of 670 nm (λ_{max}).

III. Results And Discussion

3.1 X-ray diffraction studies

XRD is the effective means to determine whether or not theCrionsaredopedintoTiO$_2$crystallattice.Figure 1 showsthe XRD patterns of Cr-doped and pure TiO_2 samples. All of the synthesized samples can be well indexed to the anatase phase. The peaks at 25.33,36.89,37.83,38.64,48.99,53.94,and55.14canbeascribed to(101),(103),(004),(112),(200),(105),and(211)planesof anatase,respectively(JCPDFCardNo.65-5714).Asnoseparate phase is detected, the doped Cr ions do not exist in the formof Cr_2O_3 or other Cr(VI) species.Compared with the undoped TiO_2, the full width at half maximum (FWHM) of the XRD peaks becomes larger for the doped samples (Figure1), indicating that introduction of Cr ions can lead to a decrease in the crystallite size of TiO_2.

The crystallite size can be calculated using the Debye–Scherrer equation –

$$d = \frac{k\lambda}{\beta cos\theta} \qquad (1)$$

where, λ is the wavelength of the X-ray radiation (k= 0.15406 nm), k is usually taken as 0.89, and β is the line width at half-maximum height of the main intensity peak after subtraction of the equipment broadening.

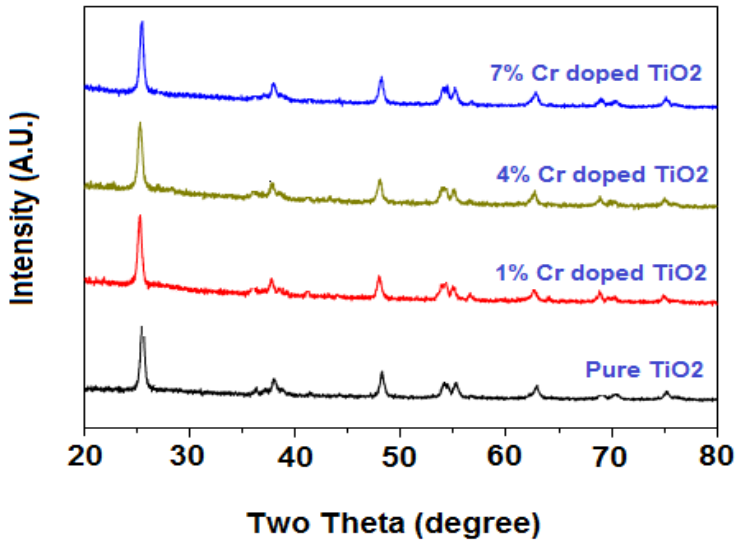

Figure 1 XRD pattern of pure and Cr doped TiO_2.

3.2 TEM analysis

TEM (Figure 2) measurements were carried out to study the surface features of the pure and doped TiO_2 samples.TEMmicrographsalsodemonstrated that the synthesized nanoparticles were homogeneous,with no significant phaseseparationsonthesurface.Both, pure and doped TiO_2 samples were composed of large quantity of well-dispersed spherical nanoparticles with uniform size and shape with average size estimated from the TEM image of 19.8 and 10.8 nm, respectively. The introduction of chromium into the TiO_2 lattice attenuates agglomeration and grain growth that could improve the photocatalytic performance and the potential application on the removal of wastewater pollutants of the doped catalyst. A similar effect has also been described in Cr^{3+}-doped TiO_2 nanoparticles synthesized by a microwave technique [28].

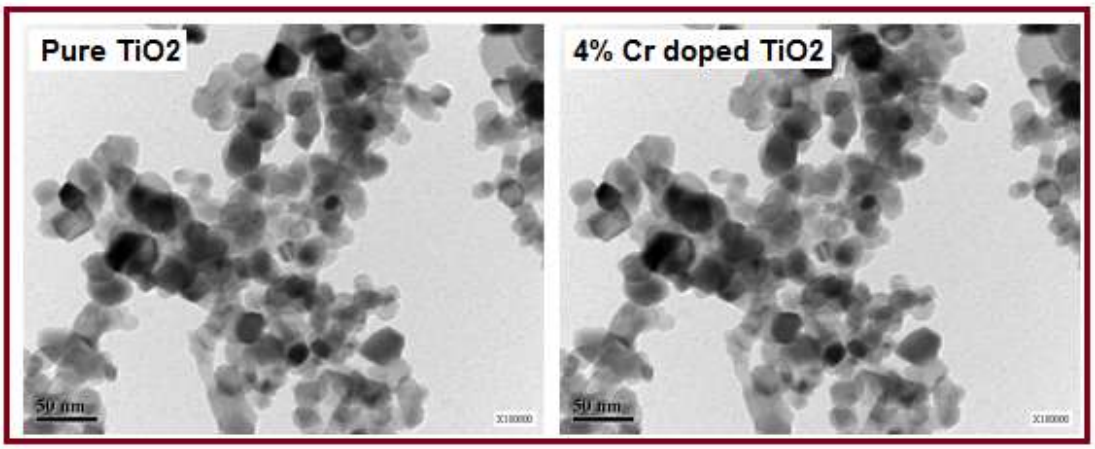

Figure 2. TEM micrographs of pure TiO_2 and 4% Cr doped TiO_2 samples.

3.3 Photoluminescence Spectra

PL spectra of pure and Cr doped TiO_2 samples are obtained using xenon flash lamp having excitation wavelength of λ_{ex}= 345 nm as shown in Figure 3. PL spectroscopy gives information related to lattice defects, oxygen vacancies, and charge trapping that can be greatly influenced by ion doping. Thus, PL spectroscopy was used to investigate the Cr (III) doping behaviour in TiO_2. Two maximum centered at 463 nm and 571 nm were found in samples. No new peaks were observed for the doped sample, indicating that the doping of Cr into TiO_2 lattice did not formed new defects related to PL emissions. In agreement with previous studies [29] it was noted the decrease in the emission intensities after Cr doping. Thus, these results confirmed that the doped Cr^{3+} ions (3d24s1) can capture photogenerated holes to form more stable Cr^{4+} or Cr^{6+} ions and decrease the recombination

rate of these separated charges [30]. Moreover, the weak UV shoulder at 396 nm and the peaks at 414, 419, and 436 nm in undoped TiO_2 are diminished with the addition of Cr(III) dopant in TiO_2, which further supports the shifting of the absorption spectra from the UV region to the visible region[29].

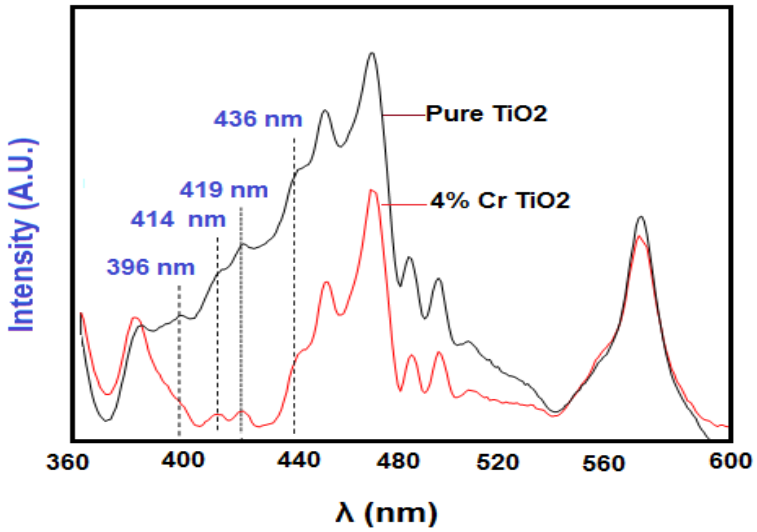

Figure 3.PL spectra of pure and 4% Cr doped TiO_2 at room temperature.

3.4 BET Analysis

As shown in Table 2, specific surface area (BET) was higher for Cr doped TiO_2 than for pure TiO_2 sample. Large surface areas are advantageous as allows an increased adsorption of pollutant molecules on the active surface sites. Both samples are mesoporous with an average pore diameter is in the range between 54.7 and 77.4 Å for pureand Cr doped TiO_2samples.

Table 2 Specific surface area and pore diameter of pure and Cr doped TiO_2 samples.

Sample	Surface Area(m^2/g)	Pore Diameter(Å)
TiO_2	52.2	54.7
TC-1	57.6	59.4
TC-4	63.9	77.4
TC-7	53.1	56.7

3.5 UV-vis absorption spectra

Forthestudyof the optical properties of synthesized samples,aclassicmethodofUV absorptionspectroscopywasapplied.Allspectraweremeasured at roomtemperatureinthesamegeometryandthesame experimentalconditions,andtheresultswerecomparedusing standardstatisticaltreatmentroutines.TheabsorptionspectraofpureandCr-dopedTiO_2 samples shown in Figure 4 arequitedifferentbothfor pure and Cr doped TiO_2, indicatingasignificanteffectof on the properties of TiO_2 nanocrystallites.

Near the UV absorption edge the absorptionpeaksareobserved for anatase TiO_2 samples at 2.91 eV. This suggests that the UV-absorption peaks can be associated with the existence of defect levels inside the band gap. The calculatedenergyof theTiO_2 lowestphonon-assistedindirectallowed(IA)transitionfrom the valenceband(VB)totheconductionband(CB)is2.91eV [38]. We assumed thatinourcasetheUVabsorption peak at2.91eVcanbeassignedtooverlapping ofthelowest-energyfundamental absorptionandabsorptionbyTi^{3+} localizedstates.In theabsorptionspectraofthestudiedsamples, spectral featuresat3.05 and 3.19 eV markedbyarrows, aredistinguishedbychangingtheslopeofthetangenttoabsorption curve.Thesefeatures,accordingtotheoreticalpredictionsofDaude et al. [31], canbeassociatedwiththefundamentalorintrinsic absorptionofanataseTiO_2.

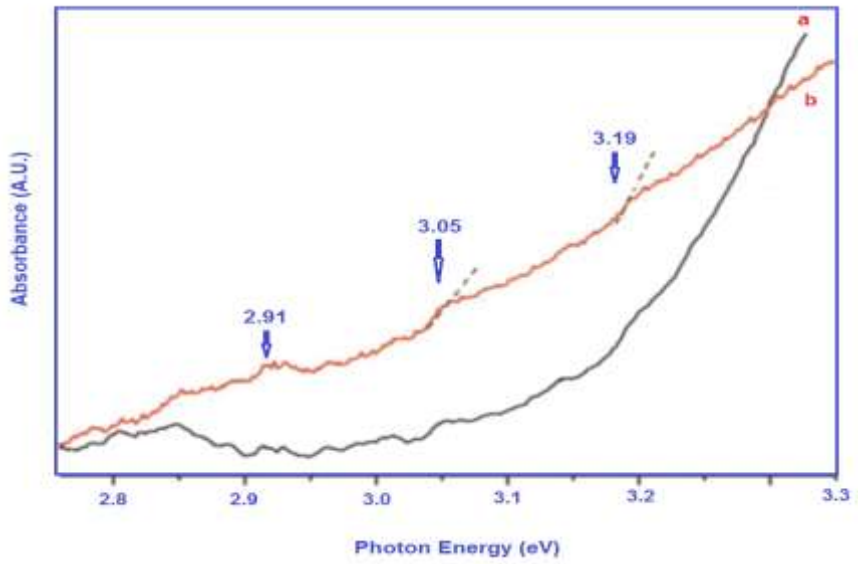

Figure 4.UV–vis absorptionspectraof a) pure TiO_2 and 4% Cr doped TiO_2.

IV. Photocatalytic activity of pure and Cr-doped TiO_2 materials

Photocatalytic activity of synthesised pure samples was determined by investigating the degradation of MB dye under the UV-light and sunlight exposure.

4.1 Effect of Catalyst

The photocatalytic activity of the synthesized samples was evaluated by measuring the photodegradation of MB as a function of irradiation time under UV light. The prepared MB solutionwas having intense absorption at 664 nm. The MB solution with 0.4 g/L catalyst dose was stirred well and allowed to UV light irradiation at regular intervals and the corresponding absorption spectra were measured.

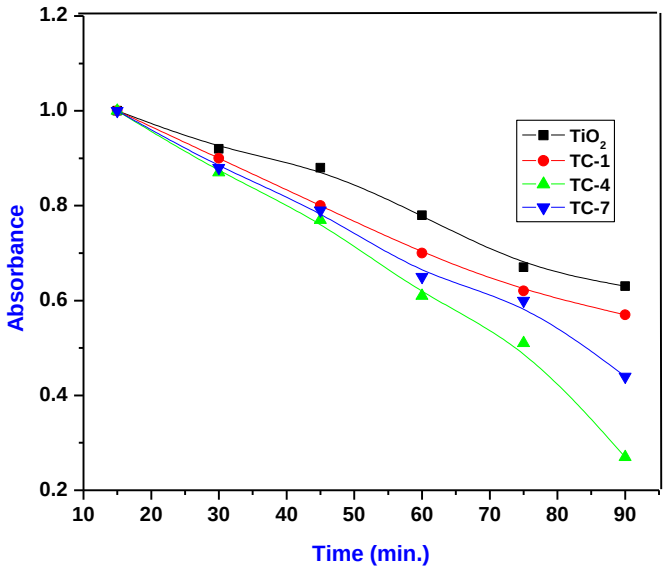

Figure 5. Degradation of MB dye with pure and Cr-doped TiO_2.
($[MB]_o$ = 20 mg/L, Catalyst dose = 0.4 g/L, pH=9.5, light intensity = 50.0 mW/cm^2)

Figure 5 shows the comparative graph for degradation of MB dye with pure and Cr-doped TiO_2 nanoparticles under UV light. The results show that higher the irradiation time, more is the decolorization of dye and lesser is the absorbance. Therefore the study also reveals that the photocatalyst can degrade the dye to maximum extent in 90 min. Photocatalytic activity of Cr-doped TiO_2 sample was found more than pure TiO_2 nanoparticles indicating the modification in the band gap. The high photocatalytic efficiency of the Cr-doped

TiO_2 canbe attributed to the reconstructed favorable surface structure withthe incorporated Cr–O–Ti bonds and their structure withhigh surface area, which is able to facilitate adsorption of watercontaminants and effective utilization of UV light. With the same calcinationtemperature, the surface area of Cr-doped TiO_2 was significantlylarger than that of the undoped one. The highest photocatalytic activity was observed for anatase TC-4 sample with the largest surface area (63.9m^2/g) and pore diameter (77.4Å).

4.2 Effect of Catalyst load

Figure 6 indicates that the rate of photocatalytic degradation of MB under UV light increases as the dose of catalyst is increased from 0.1 g/L to 1.0 g/L dueto the increased surface area and hence greater number of active sites available for adsorption of dye molecules.However, further increase of catalyst concentration results in lower photocatalyticdegradation which can be attributed to light scatteringcaused by the turbidity of the solution.

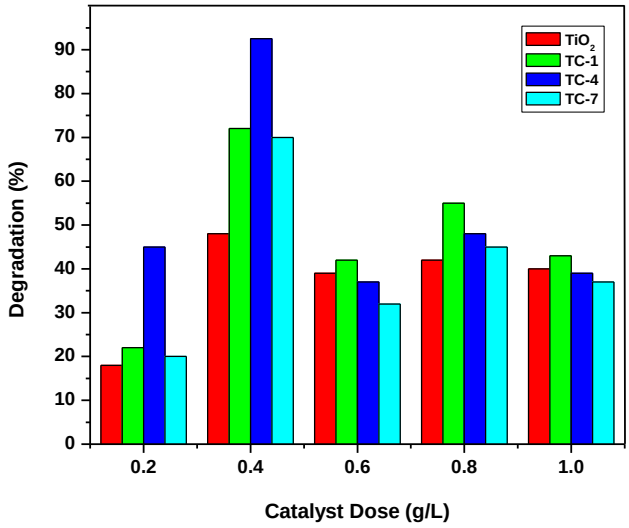

Figure 6 Photocatalytic degradation of MB dye as a function of catalyst dose. ([MB]o = 20mg/L, pH=9.5, light intensity = 50.0 mW/cm^2)

4.3 Effect of the initial dye concentration

Figure7 shows that the photodegradation of MBdye increases initially as the initial concentrationof MB is increased from 10 to 20 mg/L and then goes on decreases as the initial concentrationof MB is increased from 20 to 50 mg/L. The lower degradationefficiency at higher initial concentration can be attributed to thefact that the higher MB concentrations could absorb more photons,which reduces the available photons to activate the TiO_2which resultsin reduced degradation efficiency [32].

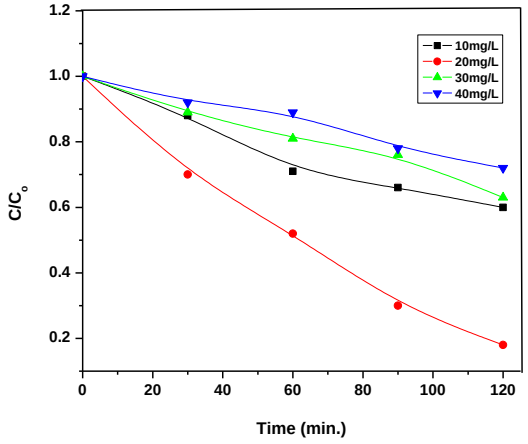

Figure 7 Effect of initial concentration of MB on the photodegradation of MB dye under UV light. (Catalyst dose = 0.4 g/L, pH = 9.5, light intensity = 50.0 mW/cm^2)

4.4 Effect of oxygen purging

The effect of air, oxygen and nitrogen bubbling on the degradation of MBdye under UV light is illustrated in Figure 8, where the rate of MB degradation in oxygen bubbling solution is three times higher than that innitrogen bubbling solution. This implies that oxygen plays a critical role insolar TiO_2based photocatalysis, enhancing the degradation efficiency evenunder lower concentration (20% oxygen in air, i.e. static oxygen).

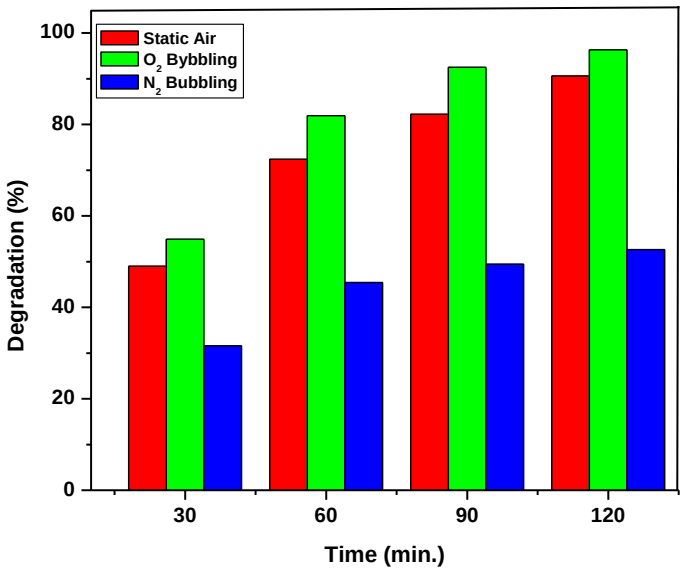

Figure 8.Effect of gas purging on the photocatalytic degradation of MB under UV light. ([MB] =20 mg/L, Catalyst dose = 0.4 g/L, pH= 9.5,light intensity=50.0 mW/cm^2).

4.5 Effect of increase in temperature

The effect of increasing temperature was observed on the photodegradation of MB dye for the sample TC-4 and Degussa P25 by varying the temperature from 298 to 328 K, keeping the dye concentration constant at 20mg/L with a catalyst concentration of 0.4 g/L. The results are graphically evaluated by Arrhenius based temperature dependence of the photocatalytic degradation by a plot of log (C_o/C) versus 1/T (Figure 9). One can see that, for TC-4 and Degussa P25, the rate of MB degradation increases but recorded as a higher for synthesized sample TC-4. Here we, assumed that, doping with Cr is significant for enhancement of photocatalytic activity of TiO_2.

It can be seen that with increasing temperature, the rate of the reaction increases which is due to the reason that increase in temperature helps to speed-up the velocity of both the hydroxyl radicals and the dye molecules to interact with each other thus the reaction competes more efficiently with the electron-hole recombination.

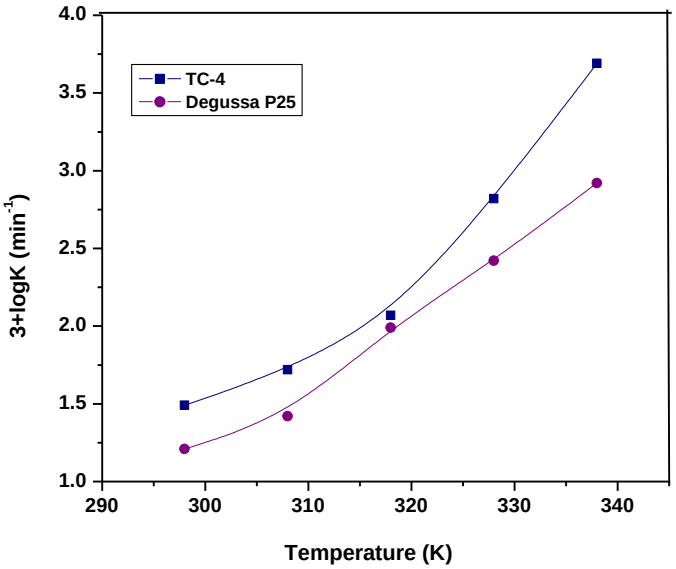

Figure 9.Effect of temperature on the photodegradation of MB dye over sample TC-4 and Degussa P25.

V. Conclusion

In summary, doping Cr in TiO_2 was successfully carried out by EDTA-Glycol method. XRD pattern suggests that TiO_2 isnot changed its structure by Cr doping. The optimized condition for the bestphotoresponse of TiO_2 in visible light is obtained by doping with the atomic ratio of Cr to Ti as 4%. The photocatalytic degradation of MB solution by Cr-doped TiO_2 photocatalysts was experimentally investigated by using UV-vis spectrophotometry. From kinetic studies it was found that the method of photodegradation is dependent on parameters such as catalyst loadings, initial dye concentration, oxygen purgingand temperature. TiO_2 itself shows lessdegradation rate than Cr-doped TiO_2 when the irradiation time is upto 90 min. These results imply thatdoping Cr in TiO_2 can improve the photocatalytic activity due to narrowed band gap energy can be scaled-up for enhancement of photocatalytic degradation under UV light for industrial applications.

References

[1]. Daghrir R, Drogui P, Robert D. *Industrial and Engineering Chemistry Research*, 2013; (**52**):3581- 3599.
[2]. Pelaez M, Nolan N.T, Pillai S.C, Seery M.K, Falaras P, Kontos A.G, Dunlop P.S.M, Hamilton J.W.J, Byrne J.A, O'Shea K, Entezari MH, Dionysiou D.D. *Applied Catalysis B: Environmental*, 2012;**(125)**:331-349.
[3]. Wang R, Jiang G, Ding Y, Wang Y, Sun X, Wang X, Chen W. *ACS applied materials & interfaces*, 2011;**(3)**:4154-4158.
[4]. Jiang G, Wang X, Zhou Y, Wang R, Hu R, Xi X, Chen W.*Materials Letters*, 2012;**(89)**:59-62.
[5]. Zhao,J.C,Wu,T.X,Wu,K.Q,Oikawa, K,Hidaka, H, Serpone, N.*Environ. Sci. Technol.*, 1998;**(32)**:2394-2400.
[6]. Yin,M. C, Li, Z. S, Kou, J. H,Zou,Z. G. *Environ. Sci. Technol*., 2009;**(43)**:8361-8366.
[7]. Fung, A. K. M, Chiu, B. K. W, Lam, M. H. W. *Water Res.*, 2003:**(37)**:1939-1947.
[8]. Hattori, A, Yokihisa, Y, Tada, H, Ito, S.*J. Electrochem. Soc.*, 2000;**(147)**:2279-2283.
[9]. Wu,C.H. *Chemosphere*, 2004; **(57)**: 601-608.
[10]. Kim, Y.J, Gao, B, Han, S.Y, Jung, M.H, Chakraborty, A.K.Ko, T,Lee,C,Lee, W. I. *J.Phys.Chem.C*,2009;**(113)**:19179-19184.
[11]. Asahi, R,Morikawa, T, Ohwaki, T,Aoki, K,Taga, Y. *Science*, 2001;**(293)**: 269-271.
[12]. Livraghi, S, Paganini, M.C,Giamello, E, Selloni, A,Di Valentin, C, Pacchioni, G.*J.Am. Chem. Soc.*, 2006;**(128)**:15666-15671.
[13]. Zhao, W,Ma, W.H,Chen, C.C,Zhao, J.C,Shuai, Z.G. *J. Am. Chem. Soc.*, 2004;**(126)**:4782-4783.
[14]. Yu, J. C, Yu, J. G, Ho, W. K, Jiang, Z.T, Zhang, L.Z.*Chem. Mater.*, 2002;**(14)**:3808-3816.
[15]. Wang,W. L, Shang, Q.K, Zheng, W, Yu, H,Feng, X.J, Wang, Z.D, Zhang, Y.B, Li, G.Q.*J. Phys. Chem. C*, 2010;**(114)**:13663-13645.
[16]. Sakatani, Y, Ando, H, Okusako, K, Koike, H,Nunoshige, J,Takata, T, Kondo, J.N, Hara, M, Domen, K.*J. Mater. Res*., 2004;**(19)**: 2100-2108.
[17]. Klosek, S, Raftery, D.*J. Phys. Chem. B*, 2001;**(105)**: 2815-2819.
[18]. Shi,J.Y, Leng, W.H, Zhu, W.C, Zhang, J.Q, Cao, C.N.*Chem. Eng. Technol*., 2006;**(29)**:146-.
[19]. Pan, L,Zou, J. J,ZhangX. W,Wang, L,*Ind. Eng. Chem. Res*., 2010;**(49)**: 8526-.
[20]. Murakami, N,Chiyoya, T,Tsubota, T,Ohno, T,*Appl. Catal., A*, 2008;**(348)**: 148-.
[21]. Buddee, S.Wongnawa, S.Sirimahachai, U.Puetpaibool, W.*Mater. Chem. Phys*., 2011;**(126)**:167-.
[22]. Jaimy K.B, Ghosh S, Sankar S, Warrier K.G.K,*Materials Research Bulletin*,2011;**(46)**:914-21.
[23]. Ould-Chikh S, Proux O, Afanasiev P, Khrouz L, Hedhili M.N, Anjum D.H, Harb M, Geantet C, Basset J.M, Puzenat E. *Chem.Sus.Chem*.2014;**(7)**:1361-1371.
[24]. Fan X, Chen X, Zhu S, Li Z, Yu T, Ye J, Zou Z. *Journal of Molecular Catalysis A: Chemical*,2008;**(284)**:155-160.
[25]. Tian B, Li C, Zhang J.*Chemical Engineering Journal*,2012;**(191)**:402-409.
[26]. Pedraza-Avella J.A, López R, Martínez-Ortega F, Páez-Mozo E.A, Gómez R. *Journal of Nano Research*,2009;**(5)**:95-104.

[27]. Vijayalakshmi K, Jereil S.D. *Journal of Materials Science: Materials in Electronics*, 2015;**(26)**:3790-3796.
[28]. Khan H, Swati I.K. *Industrial & Engineering Chemistry Research*,2016;**(55)**:6619-6133.
[29]. Li X, Guo Z, He T. *Physical Chemistry Chemical Physics*, 2013;**(15)**:20037- 20045.
[30]. Daude,N. Gout, C.Jouanin, C.*Phys. Rev. B*,1977; **(15)**:3229-3236.
[31]. Muniandy,S.S. Kaus,N.H.M. Jiang,Z.-T. Altarawneh, M. Lee,H.L. *RSC Adv*, 2017;**(7)**:48083–48094.

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