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STRUCTURAL,OPTICAL AND PHOTOCATALYTIC ACTIVITY STUDIES OF COBALT DOPED TiO_2 NANO THIN FILMS

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ABSTRACT

The structural, morphological, optical and photocatalytic properties of the cobalt doped TiO_2 films were studied using different techniques. Device quality coated TiO_2 thin films were prepared using by simple sol-gel technique by the various amount of dopants (0 to 15% of Co). The coated films have been characterized by different techniques such as XRD and EDAX and optical absorption studies for further investigation which is essential to make full use of their active properties. TiO_2 thin films of different thickness were prepared by using the sol-gel technique. XRD shows that the as deposited films are exhibit anatase crystalline structure. The optical transmittance of the film prepared in this work studied n the range of 190 to 2500 nm with direct band transition and band gap energy value equals to 3.4 ev. The photocatalytic of the film were studied by TiO_2 and Co doped TiO_2. The films were dipped in tannery effluent with different time interval. The carbonate, chloride and sulphate present in different concentrations the remaining effluent were analyzed by conventional methods. It is found that increases the catalytic activity while increases dopant concentration.

Keywords: Cobalt, Titanium oxide, Sol-gel method, Structural Properties, Optical Properties, Photocatalytic activity, carbonate, chloride and sulphate.

INTRODUCTION

Nowadays effluents coming out from various industries have mixture contains hydrochloric acid, soap oil, caustic soda, peroxide, chlorides and sulphates. These emitted effluents are disposed directly into the water sources [1] and make several problems to environment, so our prime task to disposal of these emitted effluents. Recently, many workers [2-4] have been initiated to use TiO_2-based photocatalysts for the degradation of effluents. Many authors [5-8] working to use TiO_2 thin films for photocatalytic applications due to the TiO_2 based photocatalysts play vital role than the other photocatalysts. This photo catalysis is not readily available as such but they are easy to prepare, environment-friendly and low cost.

Among the three phases of TiO_2 thin films, anatase is the most active polymorphs as photo catalyst due to its unique structure, which contains more defects; could hold more oxygen vacancies via electron trapping[9]. TiO_2 thin films are prepared by various techniques, among them electrochemical[10], continuous reaction [11], multigelation[12], spin coating [13], dip coating [14], SILAR [15], chemical vapor deposition [16], aerosol pyrolysis [17] and sol-gel [18-20] methods are important. However, TiO_2 thin films prepared from sol–gel based dip and drive coating method gives nano particles with high purity at relatively low temperature. This unit is very simple, compact and maintenance free set up. The dip and drive mechanism is very easily adjustable, to obtain uniform, homogeneous, and crystalline thin films with required thickness. As pre-heating and post heating arrangements are available in this unit, removal and fixing of substrate for pre and post heating respectively carried out in conventional thin film deposition process could be avoided resulting in enhanced quality and productivity.

The possibility of stoichiometry controlling process, easy step for the composite preparation and production of homogeneous materials have driven many researchers to use this method for preparing TiO_2 thin films. This crusade of researches on sol–gel based dip and drive preparation methods of TiO_2 thin films has provided the push for the present study. However, use of pure nanocrystalline TiO_2 thin films is significantly constrained because of its wide band gap, low efficiency of sunlight utilization and high recombination rate of electrons-holes. The effective photoexcitation of TiO_2 semiconductor particles requires the application of light with energy equal to or higher than its band gap energy. But it is commonly reported that anatase phase of TiO_2 with a band gap (E_g) of 3.2 eV is more efficient as a photocatalyst than rutile phase [21].

Many investigators [22–25] recently investigated the effects of doping various materials to enhance the catalytic activity. Especially the incorporation of transition metal ions into the TiO_2 crystal lattice may alter the photoreactivity appreciably by shifting the band gap of the catalysts into the visible region. Therefore, it is of great interest to improve the photocatalytic activity of nanocrystalline TiO_2 thin films to enhance the practical applications of TiO_2 thin film based photocatalysts [26]. Compared with all other transition metals cobalt exhibit superior photodegradation capability under visible light irradiation [27, 28]. Co-doped TiO_2 thin films exhibit not only visible-light derived photo degradation but also liquid-phase adsorption ability of effluents in aqueous solution. Preparation of Co doped TiO_2 thin films by sol-gel method have not been available. Hence in the present research pure and Co- doped TiO_2 thin films were prepared and characterized the photocatalytic degradation activities of Tannery effluent under UV-Vis light.

EXPERIMENTAL

The TiO_2 thin films have been prepared by simple sol-gel method. Titanium isopropoxide TIP (Alfa Aaser 99.9%) has been used as a titania precursor, absolute ethanol (Aldrich 99.9 %) used as a solvent to prepare the sol and acetic acid as a catalyst to control the pH of the solution. Titanium isopropoxide (1.5 ml) is added drop wise into 20ml ethanol with constant stirring. After thirty minutes stirring, acetic acid is added to achieve the desired pH of the solution. The final solution is aged for thirty minutes at air atmosphere.

Optically transparent clean glass slides were used as substrates. The cleaned substrates were dipped in the solution for few seconds and dried at 100°C for 5 minutes and then allowed to cool to room temperature. TiO_2 was again dip coated on the already coated TiO_2 film and heated at 100°C for 5 minutes and then allowed to cool to room temperature. Similarly the dipping and drying process was repeated for several times to get the thicker films. The heating of the film after each dipping in air is carried out to enhance the inorganic polymerization and stabilize the mesophases involved. The films were then dried at room temperature for 2 h. Then the as-coated films have been annealed at 550°C for 1 hour in air using a heating rate of 2° C/min.

To prepare cobalt doped TiO_2 thin film, different percentage (5%, 10%, 15%) of cobalt nitrate [Co $(NO_3)_2$] were dissolved in 5ml ethanol solution separately and then added drop wise to the mixture of titanium isopropoxide and ethanol. The cleaned glass substrates were dipped, dried and annealed in the similar way as mentioned above prepare the different size of cobalt doped TiO_2 thin films.

RESULTS AND DISCUSSION

Structural Properties of Pure and Co doped TiO_2 Thin Films

Figure1 shows the X-ray diffraction patterns of pure and Co doped TiO_2 thin films annealed at 550°C. The films exhibit small peaks indicating the formation of nanocrystalline TiO_2 films. The peaks are not sharp indicating that the average crystallite size is small. Due to size effect the peaks in the diffraction pattern broaden and their widths become large as the particles become smaller. The peaks have been indexed and found to be that of anatase TiO_2. The presence of peak at $2\theta = 25.38^{\circ}$ (d spacing is 3.505A) corresponding to (101) plane and it is the characteristic peak of anatase phase (JCPDS 21-1272). The X-ray diffraction pattern of Co doped TiO_2 thin films show no much changes compared with the X-ray diffraction pattern of pure TiO_2 thin films, which confirms that there is no additional phase formation but there is a reduction of particle size. Close observation of the X-ray diffraction pattern of Co doped TiO_2

thin films show shift of peak towards high angles. The crystallite size has been calculated from the integral width of the diffraction peaks using Scherrer formula $D=k\lambda/\beta\cos\theta$, where *D* is the crystal size, the constant k is the shape factor ≈ 0.94, λ is the X-ray wavelength (1.54056 Å), β is the full width at half maximum (FWHM) of the diffraction peak (radian) and θ is the diffraction angle at the peak maximum. The calculated crystal sizes are 22 nm, 10 nm, 8.5 nm and 23 nm for the pure, 5% Co doped, 10% Co doped and 15% Co doped TiO_2 thin films respectively. The reduction of particle size is also due to the usages of acetic acid during the sol formation. Since pH of solution is close to 3, there is a good chance for protonation of TiO_2 nanoparticles which could suppress further crystallization of nanoparicles. The excess acetate anion adsorbed on the surface of TiO_2 could also suppress the growth of TiO_2 nanoparticles. This type of acetate anion complexation on the surface of anatase form of TiO_2 may be the reason for the decrease of the crystallite size of TiO_2 in the sol-gel process [30]. The addition of acetic acid did not cause residual impurities on the surface of TiO_2 after annealing. Higher amount of doping (i.e. 15% of Co) further enhances the growth and increases the particle size. No peak has been detected corresponding to the brookite and rutile phase of TiO_2. The diffractogram clearly suggesting that only anatase phase has been formed.

Surface analysis of pure and Co doped TiO_2 thin films

Figure 2 (a-d) shows the SEM images of pure and Co doped TiO_2 thin films annealed at 550°C. Pure TiO_2 thin film shows the global and uniform particles which are coherent together. Whereas 5% and 10% Co doped TiO_2 thin films shows the reduced particle sizes. Fig 2d clearly a show that 15% Co doped with TiO_2 promotes the formation of nanorod like structure.

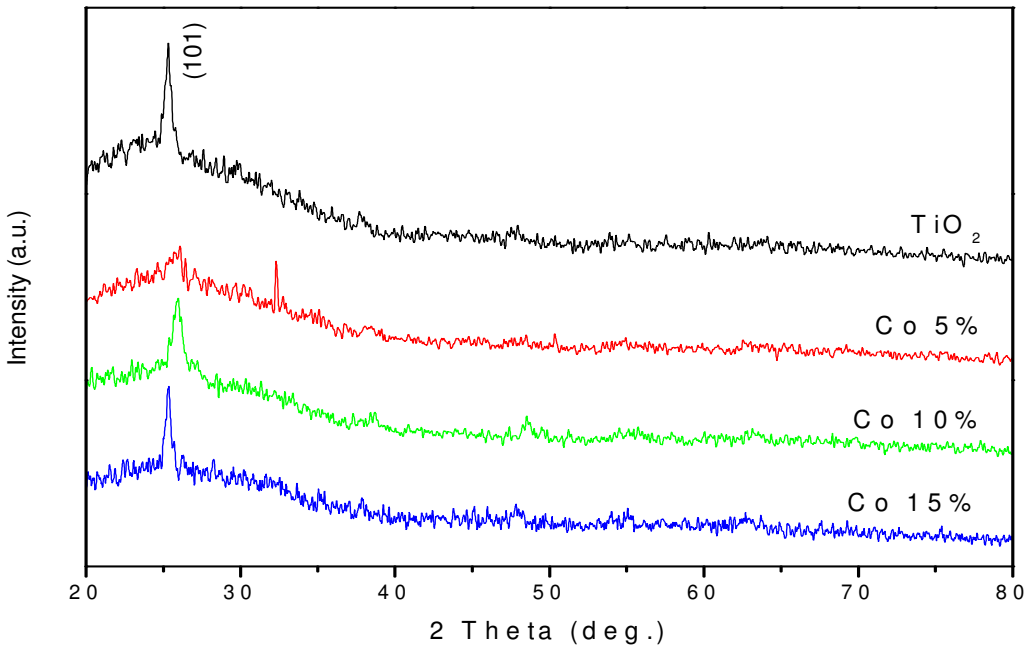

Fig.-1: X-ray diffraction pattern of pure and Co doped TiO_2 thin films

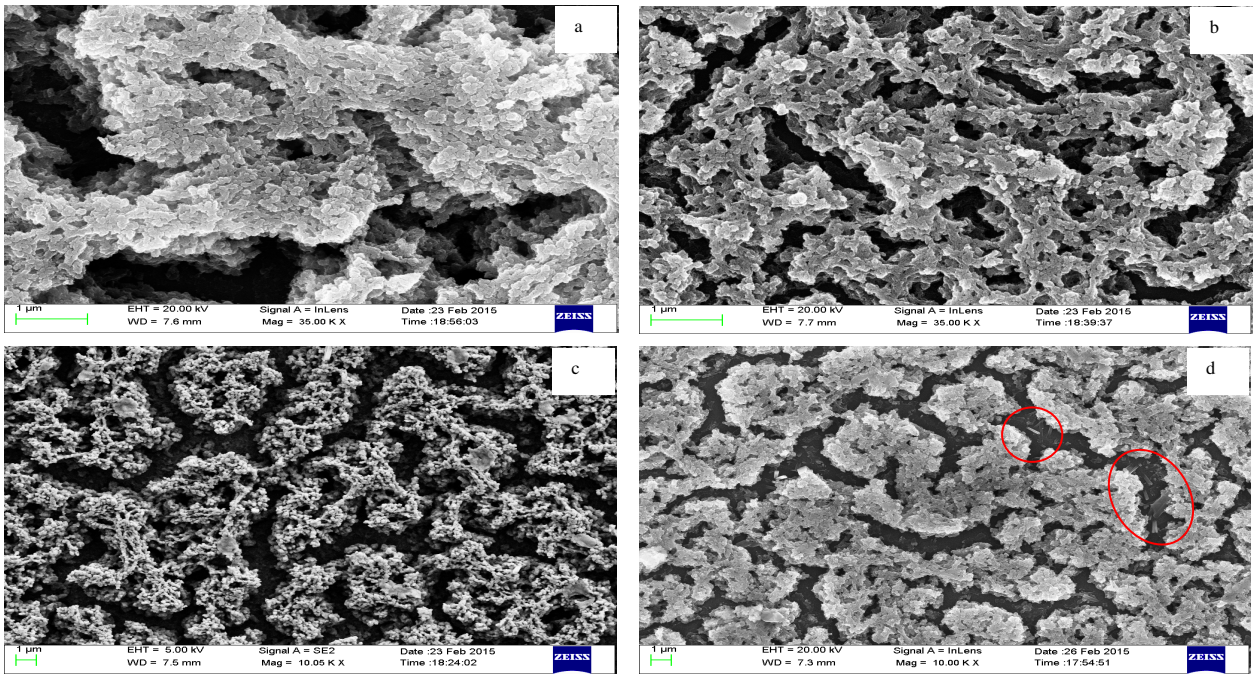

Fig.-2: SEM images of (a) pure (b) 5% (c) 10% and (d) 15% Co doped TiO_2 thin films

Figure-3 (a-d) shows the AFM images of pure and Co doped TiO_2 thin films annealed at 550°C.Figure3(a) clearly shows the presence of small crystalline grains with spaces, because of the doping well defined particle-like features with granular morphology has formed and this leads to the appearance of grains making the films to have higher surface roughness. Evaluation of surface patterns was conducted by estimating the roughness of the film (root mean square). The root mean square surface roughness of the film is found to be about 10 nm.

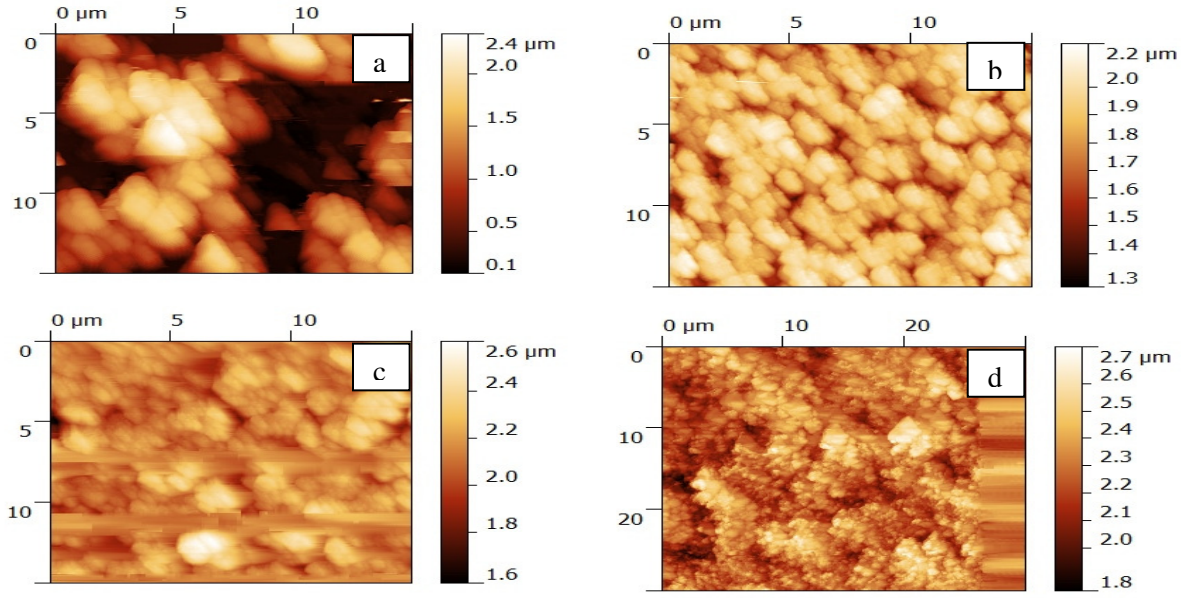

Fig.-3: AFM images of (a) pure (b) 5% (c) 10% and (d) 15% Co doped TiO_2 thin films

The overall morphology of the products was further analyzed by TEM images. The high-resolution transmission electron microscope image of the pure and Co doped TiO_2 thin film annealed at 550°C is shown in Figure 4 (a-d). The image clearly shows that pure TiO_2 thin film samples are made up of a combination of irregular shaped nanocrystals. Using the particle number (frequency %) and the average particle diameter of the particles in the high-resolution transmission electron microscope image, the particle size has been calculated and is found to be 20 nm for the pure TiO_2 thin film. This is in good agreement with the X-ray diffraction results.

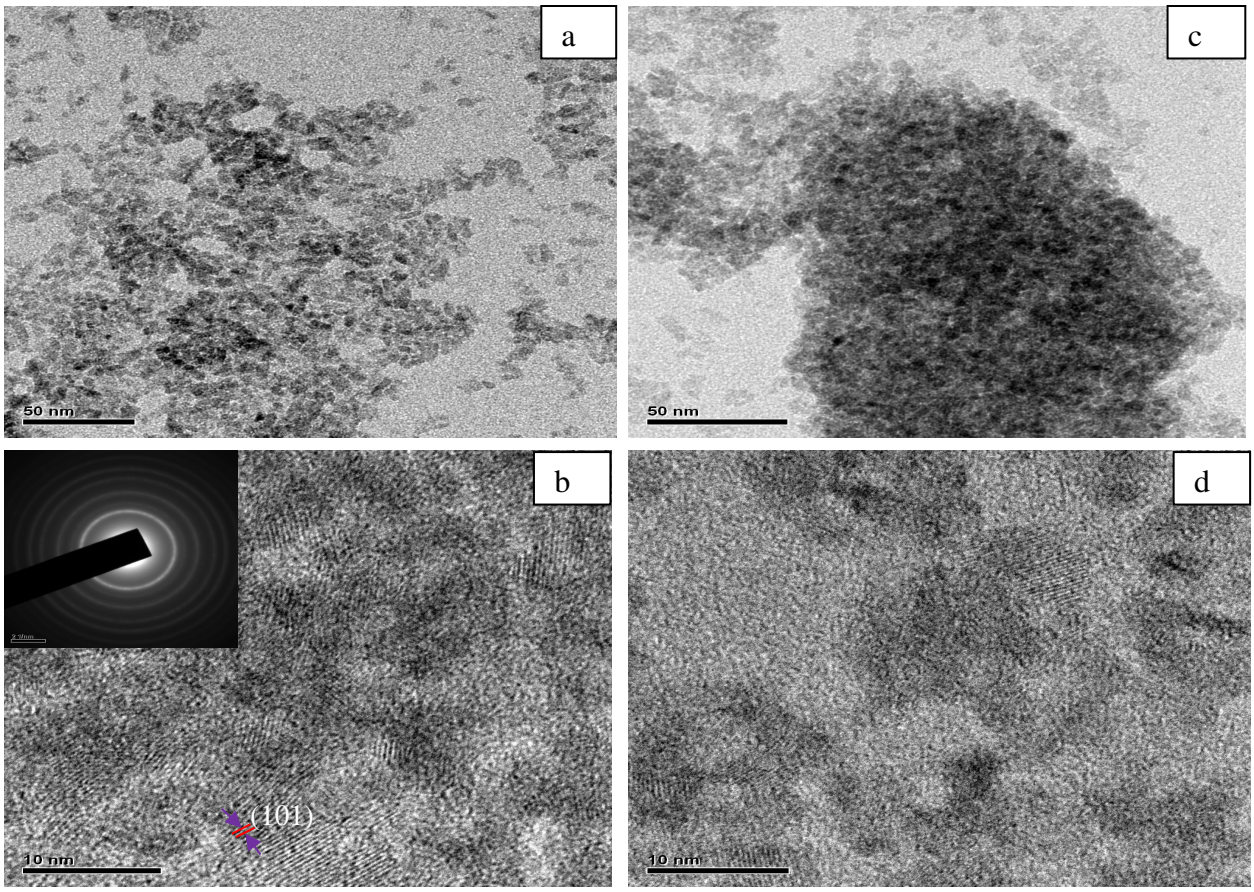

Fig.-4: TEM images of (a) pure (b) 5% (c) 10% and (d) 15% Co doped TiO_2 thin films

The inset of the Figure 4 (b) shows the SAED pattern of the pure TiO_2 thin film samples. The images (a & c) clearly show spherical and elongated shaped particles with approximately uniform in size of about 20-30nm. The high resolution images show that each of these larger particles is the agglomeration of smaller particles, with nanostructured domain. The films exhibit lattice fringes and using the fringes the d spacing has been calculated and is found to be 0.35nm. On comparing the d-spacing with standard JCPDS data it is observed that the d spacing corresponds to the (101) plane of anatase TiO_2.

Compositional Analysis of Co doped TiO_2 Thin Films

Energy dispersive x-ray analysis (EDAX) of TiO_2thin film is shown in Figure 5(a). EDAX spectra result shows the presence of Ti and O. The unidentified peak at 1.8 keV is due to presence of silicon. The origin of silicon is due to the glass substrate and presence of carbon is due to the carbon coating during SEM analysis.

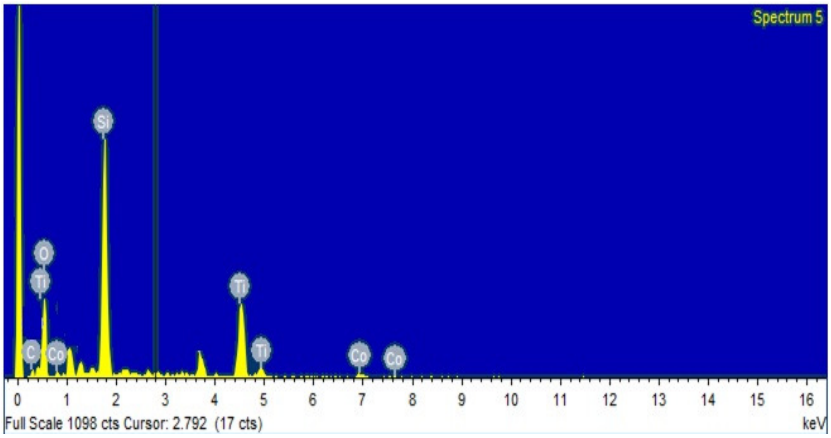

Fig.-5: EDAX pattern of 10% Co doped TiO_2 thin films

Optical Properties of TiO_2 and Co doped TiO_2 Thin Films

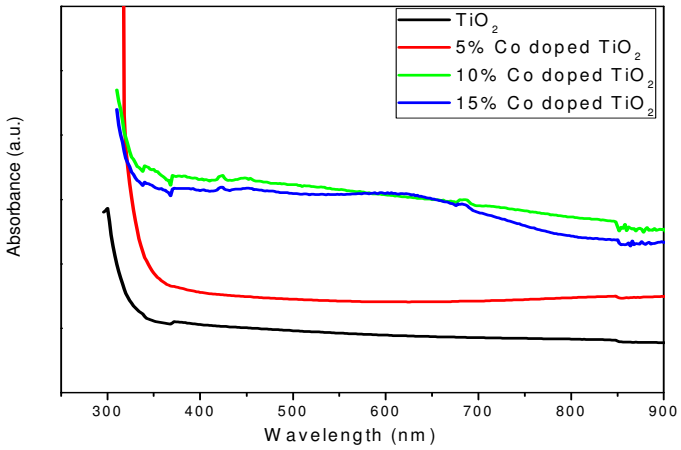

Fig.-6: UV-VIS absorbance spectra of pure and Co doped TiO_2 thin films

The absorbance spectra of pure and Co doped TiO_2 thin films annealed at 550°C are shown in Figure 6. The rapid red shift of absorbance spectra is due to the change in grain size and this has caused the onset of absorption to shift to the red end of the spectrum. A red shift of absorption edge also indicates a decrease in the band gap of TiO_2 films and this is due to the improvement of crystallinity on doping. The calculated band gap values are 3.6, 3.5, 3.2 and 3.14 eV for pure, 5%, 10% and 15% Co doped TiO_2 thin films respectively.

Photocatalytic properties of TiO_2 and Co doped TiO_2 thin films

The photocatalytic activity of pure and (5%, 10%, 15%) doped TiO2 was studied by exposing the UV light on the beakers containing effluent with thin films separately with same distance and time of exposure (1,2,3hr) then the effluents were analyzed for the amount of carbonate, chloride and sulphate present. It is found that there is a significant changes in the radicals present after 3hr duration time. The amount of radicals in the different concentrations were measured and tabulated as shown in table 1. There is no appreciable value changes in the first two exposures. This is because of the difference in the atomic radii of the elements. In case of Carbonate estimation 15% Co doped TiO_2 is best while comparing to other two concentrations and pure one. In case of Chloride 5% Co doped TiO_2 gives better result but there

is no appreciable changes between pure and this one. While in Sulphate the pure TiO_2 is best compared with doppant.

Table-1: Amount of radicals present at different concentration levels

Parameters	Solvent	TiO_2	5 % of Co-TiO_2	10 % of Co-TiO_2	15 % of Co-TiO_2
Total Hardness (mg/l)	2200	1000	1000	1000	500
Chlorides (mg/l)	1200	1000	940	975	960
Sulphates (mg/l)	82.3	20.5	42.8	43.78	41.5

CONCLUSION

Pure and 5%, 10% and 15% Co doped nanocrystalline TiO_2 thin films have been prepared by simple sol-gel method. The prepared thin films are annealed at 550°C. The grain size has been observed to decrease with the increase of Co doping concentrations. The AFM studies clearly show the formation of TiO_2 nanocrystallites on the surface. The impact of addition of dopant on surface morphology and photocatalytic activity were discussed. The optical studies revealed a red shift in the absorption edge and decrease of band gap on doping concentration.

REFERENCES

1. A.V.Rao, B.L.Jain, and I.C.Gupta, *Indian J.Environ.Health,* **35(2)**, 132 (1993).
2. U.G. Akpan, and B.H. Hameed, *Applied Catalysis A: General* **375**, 1 (2010).
3. X. Zhang, D.D. Sun, G. Li, and Y. Wang, *J. Photochem. Photobiol. A: Chem.,* **199**, 311 (2008).
4. S.H. Park, J.S. Park, S.D. Yim, S.H. Park, and Y.M. Lee, and C.S. Kim, *J. Power Sources,* **181** (2) 259 (2008).
5. H.L. Qin, G.B. Gu, and S. Liu, *Mater. Chem. Phys.,* **112**,346 (2008).
6. S. Song, L. Xu, Z. He, H. Ying, J. Chen, X. Xiao, B. Yan, and J. Hazard. *Mater.* **152 (3)**, 1301 (2008).
7. B. Mounir, M.N. Pons, O. Zahraa, A. Yaacoubi, A. Benhammou, and J. Hazard. Mater. **148 (3)**, 513 (2007).
8. N. M. Ganesan, N. Muthukumarasamy, R. Balasundaraprabhu, and T. S. Senthil, *Optoelectronics and advanced materials – Rapid Communications,* **8**, 581 (2014).
9. Y. Jiao, F. Chen, B. Zhao, H. Yang, and J. Zhang, *Colloid Surface A*, 402, 66 (2012).
10. L. Fan, N. Ichikuni, S. Shimazu, and T. Uematsu, *Appl. Catal. A: Gen.* **246**, 87 (2003).
11. K.D. Kim, H.T. Kim, and A. Colloids Surf, Physicochem. *Eng. Aspects*, 207, 263 (2002).
12. P. Krishnamurthi and E Murugan*, J. Current Pharm. Res*. **11 (1)**, 38, (2013)
13. S. Inoue, A. Muto, H. Kudou, and T. Ono, *Appl. Catal. A: Gen.* 269, 7 (2004).
14. T.S. Senthil, N. Muthukumarasamy, S. Agilan, M. Thambidurai, R. Balasundaraprabhu, *Materials Science and Engineering B*, 174, 102 (2010).
15. P. Kluson, H. Luskova, T. Cajthaml, and O. Solcov, *Thin Solid Films*, **495**, 18 (2006).
16. T. S. Senthil and Misook, and Kang, *Bull. Korean Chem. Soc.* 2013, **34(4)**,1188 (2013)
17. G. K. Boschloo, A.Goossens, and J. Schoonman, *J. Electro chem. Soc.,* **144**, 1311 (1997).
18. L.Kavan, and M.Gratzel, *Electrochem. Acta,* **40**, 643 (1995).
19. W.Que, A.Uddin, and X.Hu, *Journal of Power Sources,* **159**, 353 (2006).
20. T. S. Senthil, N. Muthukumarasamy, M. Thambidurai, R. Balasundaraprabhu, and S. Agilan, *J. Sol-Gel. Sci. Technol.* **58**, 296 (2011).
21. N. M. Ganesan, N. Muthukumarasamy, R. Balasundaraprabhu, and T. S. Senthil, *Iranian Journal of Science & Technology,* **38**, 187 (2014).
22. M.A. Barakat, H. Schaeffer, G. Hayes, and S. Ismat-Shah, *Applied Catalysis B: Environmental,* **57**, 23 (2004)

23. J. Chen, M. Yao and X. Wang, *J. Nanopart. Res.* **10**,163 (2008).
24. M. Subramanian, S. Vijayalakshmi, S. Venkataraj, and R. Jayavel, *Thin Solid Films,* **516**, 3776 (2008).
25. S. Liu, X. Chen and J. Hazard. *Mater.*, **152**, 48 (2008).
26. N. Venkatachalam, M. Palanichamy, and V. Murugesan, *J. Mol. Catal.*, A **273**,177 (2007).
27. H. Shi, T. Zhang, T. An, B. Li, and X. Wang, *J. Colloid Interface Sci.*, **380**,121 (2012).
28. J. P. Wang, H. C. Yang, and C. T. Hsieh, *Journal of Photoenergy*, **12**, 1 (2012).
29. A. Di Paola, E. Garcıa-Lopez, S. Ikeda, G. Marc I, B. Ohtani, and L. *Palmisano, Catalysis Today*, **75**, 87 (2002).
30. S.V. Elangovan, V. Chandramohan, N. Sivakumar, and T.S. Senthil, *Desalination and Water Treatment* , **8** (2015).
31. M. Hamadanian, A. Reisi-Vanani and A. Majedi, *J. Iran. Chem. Soc,*. **7**, 52 (2010).

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