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## Research Article

# SYNTHESIS AND CHARACTERIZATION OF UNDOPED AND DOPED $TiO_2$ PHOTOCATALYST

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**ABSTRACT**

Undoped and doped $TiO_2$ photocatalyst where characterized by FTIR, DRS, BET SEM and XRD. From these studies we investigated the optical absorption ($\lambda_{max}$), functional group, particle size, surface morphology and elementary composition of undoped and doped $TiO_2$. The dopants used where four atomic percentage of $Cr^{3+}$, $Fe^{3+}$.



## INTRODUCTION

Titanium dioxide or titania ($TiO_2$) was first produced commercially in 1923. It is obtained from a variety of ores. The bulk material of $TiO_2$ is widely nominated for three main phases of rutile, anatase and brookite. Among them, the $TiO_2$ exists mostly as rutile and anatase phases which both of them have the tetragonal structures. However, rutile is a high-temperature stable phase and has an optical energy band gap of 3.0 eV (415 nm), anatase is formed at a lower temperature with an optical energy band gap of 3.2 eV (380 nm) (Kheamrutai Thamaphat, 2008). Among these polymorphs, rutile and anatase have been widely studied. Brookite is rarely studied due to its complicated structure and difficulties in sample preparation (Hu *et al*., 2009). These three phases can be commonly described as constituted by arrangements of the same building block-Ti–$O_6$ octahedron in which Ti atom is surrounded by six oxygen atoms situated at the corners of a distorted octahedron. Photocatalysis using $TiO_2$ as a catalyst has been widely reported as a promising technology for the removal of various organic and inorganic pollutants from contaminated water and air because of its stability, low cost, and non-toxicity (Liu *et al*., 2008). Well-dispersed titania nanoparticles with very fine sizes are promising in many applications such as pigments, adsorbents, and catalytic supports (Ramakrishna, 2003).

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Since Fujishima and Honda discovered the photocatalytic splitting of water on a $TiO_2$ electrode under ultraviolet (UV) light, many synthesis methods for preparing $TiO_2$ nanoparticles and their applications in the environmental (photocatalysis and sensors) and energy (photovoltaics, water splitting, photo/electrochromics, and hydrogen storage) fields have been investigated (Shan, 2010). Recently, fine particles of titania have attracted a great deal of attention, because of their specific properties as an advanced semiconductor material, such as a solar cell, luminescent material, and photocatalyst for photolysis of water or organic compounds and for bacteriocidal action (Sugimoto *et al*., 2003). The Cr-doped and Fe-doped $TiO_2$ photocatalyst have consumed great attention due to its enhanced photocatalytic activity (Ibram Ganesh *et al*., 2012; Yan-Hua Peng *et al*., 2012). In this paper, we report the preparation of four atomic percentage of Cr-doped and Fe-doped $TiO_2$ photocatalyst.

### Experimental methods

### Synthesis and Photocatalyst preparation

Titanium dioxide, anatase, were purchased from sigma Aldrich and was of analytical reagent 95 grade and used without further purification. Deionised water was used in all experimental preparations. The samples were prepared by hydrothermal method (Dhanalakshmi *et al*., 2008). High temperature sintering method was adapted for the preparation of the photocatalyst.

In the case of doping, a common procedure was followed: An aqueous slurry of the semiconductore powder containing calculated amounts of transition metal salt was stirred magnetically (REMI-magnetic stirrer-2MLH) for 2 hours to distribute the metal ions uniformly upon the semiconductor powder. This slurry was then evaporated in an air oven at 100-200$^{o}$C. The dried samples were ground to fine powder, loated in a silica boat and introduced into a muffle furnace for sintering. Sintering was carried out at 450$^{o}$C for all the samples. Stepwise increases of temperature increased the effectiveness of doping (Mori *et al*., 198; Prabu, 2014). Sintering of samples was carried out in an inert atmosphere, after cooling to room temperature, the sintered samples were ground to fine powder.

**Instrumentations**

The IR-Spectrum of the metal doped photocatalyst was recorded by Bruker 3000. The UV spectrum (DRS) of the Cr doped and Fe doped photocatalyst was recorded on Varian, Cary 5000 model UV spectrophotometer. Scanning electron microscopy (SEM) measurements were performed on 'ZEISS'. The surface areas of the photocatalyst powders were measured using a BET apparatus. X-ray diffraction patterns were recorded using computer controlled XRD units (X-ray generator: PW 1130: Vertical diffractrometer: PW 1050; Diffractrometer control PW 1710; Philips, Holland).

The spectrum shows a peak at 3854–3755 cm$^{-1}$ for bare and various oxide doped $TiO_2$ nanoparticles, which was described to the both symmetric and asymmetric stretching vibrations of the hydroxyl group. Whereas, the characteristic peaks between 1638-1646 cm$^{-1}$ is associated with the O-H bending vibration of the absorbed water molecules. In the spectrum of pure $TiO_2$, the peak at 416 cm$^{-1}$ should be attributed to Ti-O bond in the $TiO_2$ lattice (anatase titanium) (Prabu, 2014). The broad intense band seen below 1200 cm $^{1}$ is due to Ti-O-Ti vibrations (Lin *et al*., 2006; Ganesh *et al*., 2012; Ganesh *et al*., 2012; Kumari *et al*., 2007; Navio *et al*., 1992; Litter, 1996; Bickley *et al*., 1992; Cordishi *et al*., 1985; Tsodikov *et al*., 1995; Wang *et al*., 1999; Ballyy *et al*., 1998). These results match very well with those reported in the literature for Fe-doped $TiO_2$ powders and for anatase and rutile phases of $TiO_2$ (Fujishima, 1972; Bak *et al*., 2002).

**Diffuse Reflectance Spectra (DRS)**

The UV-Visible diffused reflectance spectra (DRS) of the undoped and Cr, Fe doped $TiO_2$ samples are shown in **fig. (2).** The maximum absorption for all samples are observed in 337 nm from which the approximate band gap of 3.2 eV is calculated. The spin forbidden d-d transition $^{4}A_2 \rightarrow {}^{2}T_1$ and a spin allowed $^{4}A_2 \rightarrow {}^{4}T_2$ transition would be the possible explanation that be accounted for the charge transfer due to occupancy of the stable $Cr^{3+}$ in octahedral environment (Blasse *et al*., 1981; Jakani *et al*., 1985).

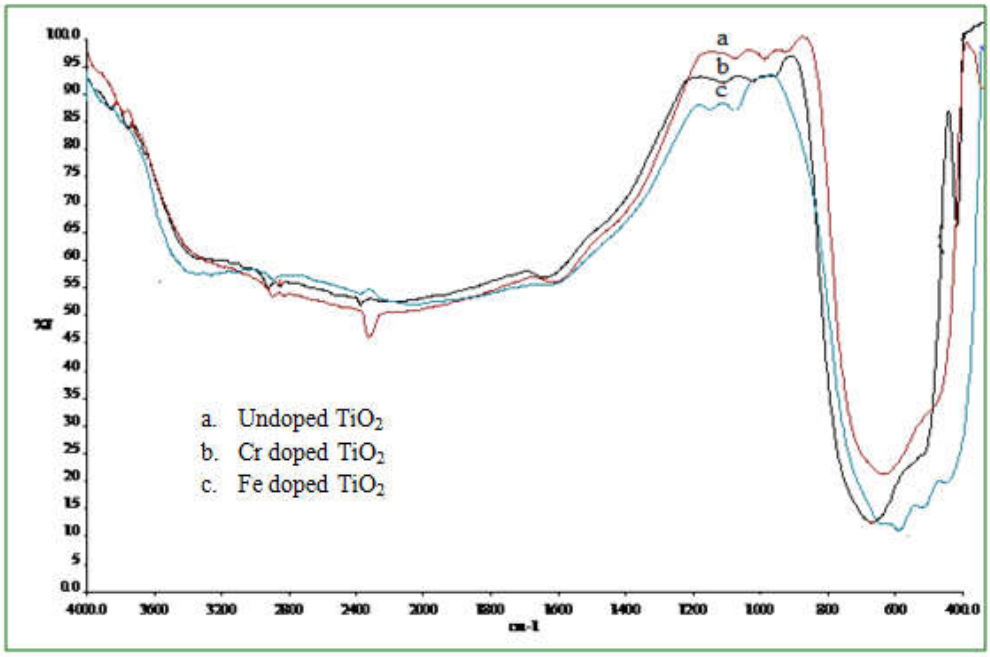


**Fig. 1 IR Spectra of undoped and metal ions $TiO_2$**

## RESULTS AND DISCUSSION

**Characterization studies**

**Fourier Transform-Infrared (FT-IR)**

The FTIR spectra of pure and various oxide doped $TiO_2$ powders were recorded in the range of 4000-400 cm$^{-1}$ using KBr pellet technique. The recorted FTIR spectrum of pure $TiO_2$, four atomic percentage Cr doped and Fe doped $TiO_2$ are shown in Fig. (1) respectively.

Doping with transition metal ions extends the absorption of the photocatalysts from the fundamental band edge higher wavelength regions. The shifts the fundamental band edges of the doped samples that the band gap is being slightly altered due to doping. This red shift of the optical absorption in doped $TiO_2$ was the outcome of d–d transition of $Fe^{3+}$ ($^{2}T_{2g} \rightarrow {}^{2}A_{2g}, {}^{2}T_{1g}$) and the charge transfer transition between interacting iron ions ($Fe^{3+} + Fe^{3+} \rightarrow Fe^{4+} + Fe^{2+}$). These $Fe^{3+}$ 3d states in addition to oxygen vacancies and $Ti^{3+}$ centers create band states, thereby favoring the electronic

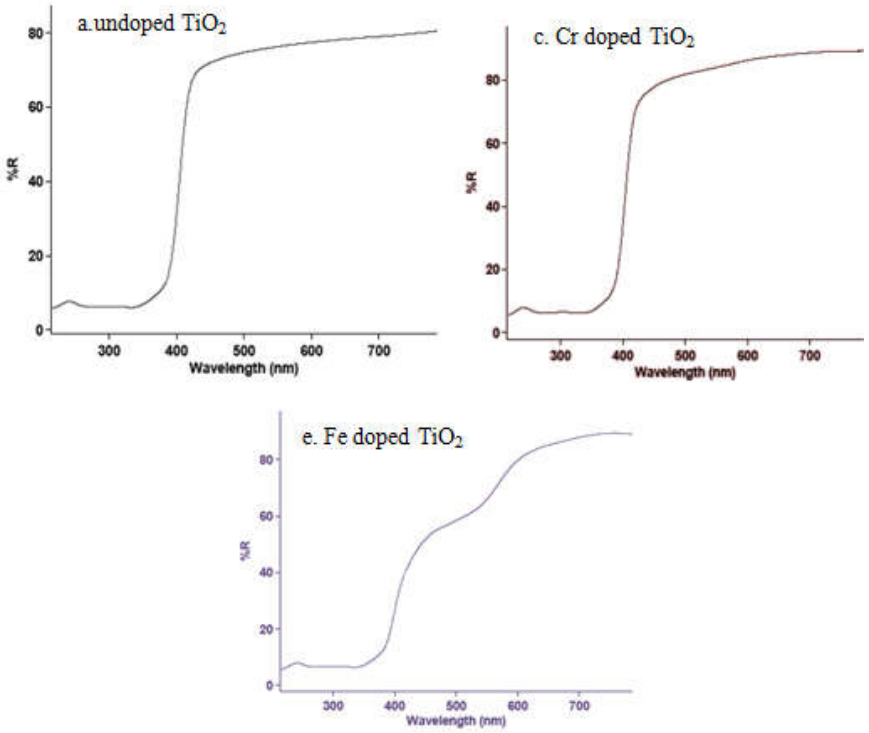


**Fig. 2. Diffuse absorption spectra of undoped and metal ions doped $TiO_2$**

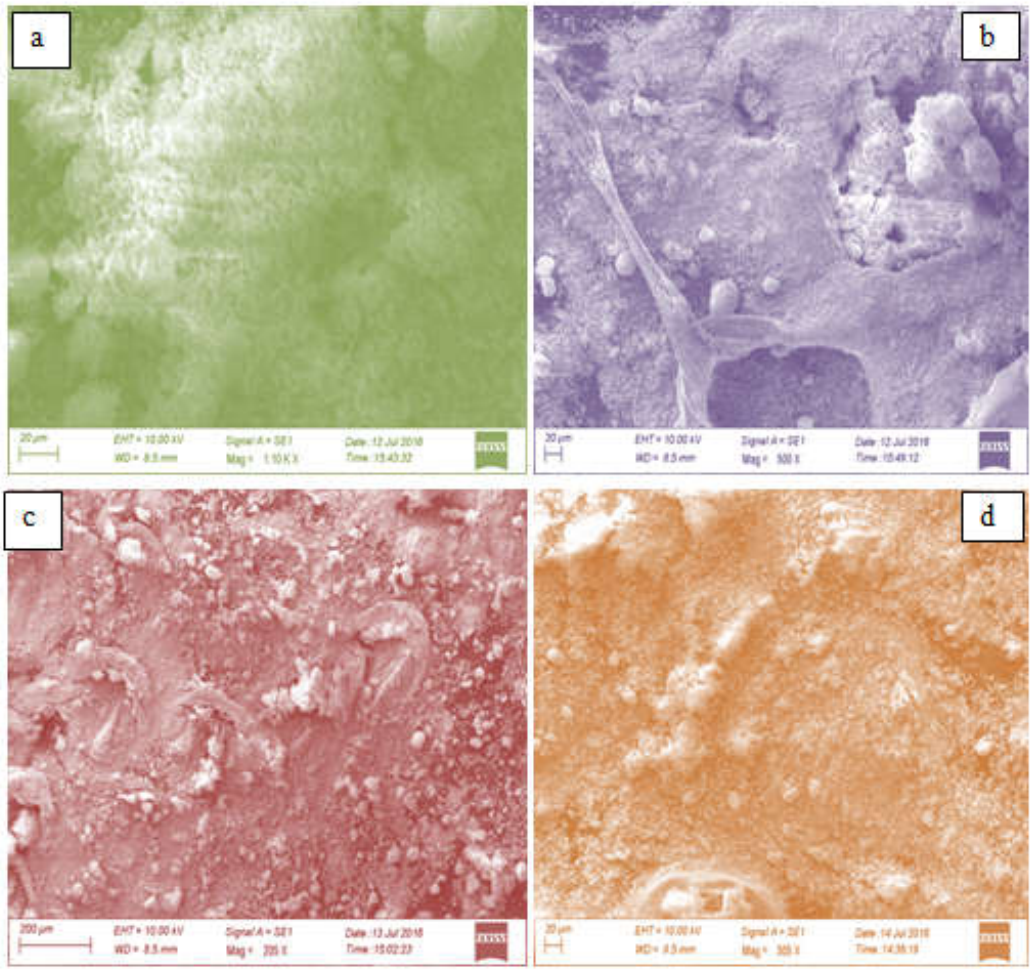


**Fig.3 Scanning Electron Micrographs of (a). Undoped $TiO_2$ (1.10 KX)**
**(b). Four atomic percentage Cd doped $TiO_2$ (500 X)**
**(c). Four atomic percentage Cr doped $TiO_2$ (205 X)**
**(d). Four atomic percentage Fe doped $TiO_2$ (505 X)**

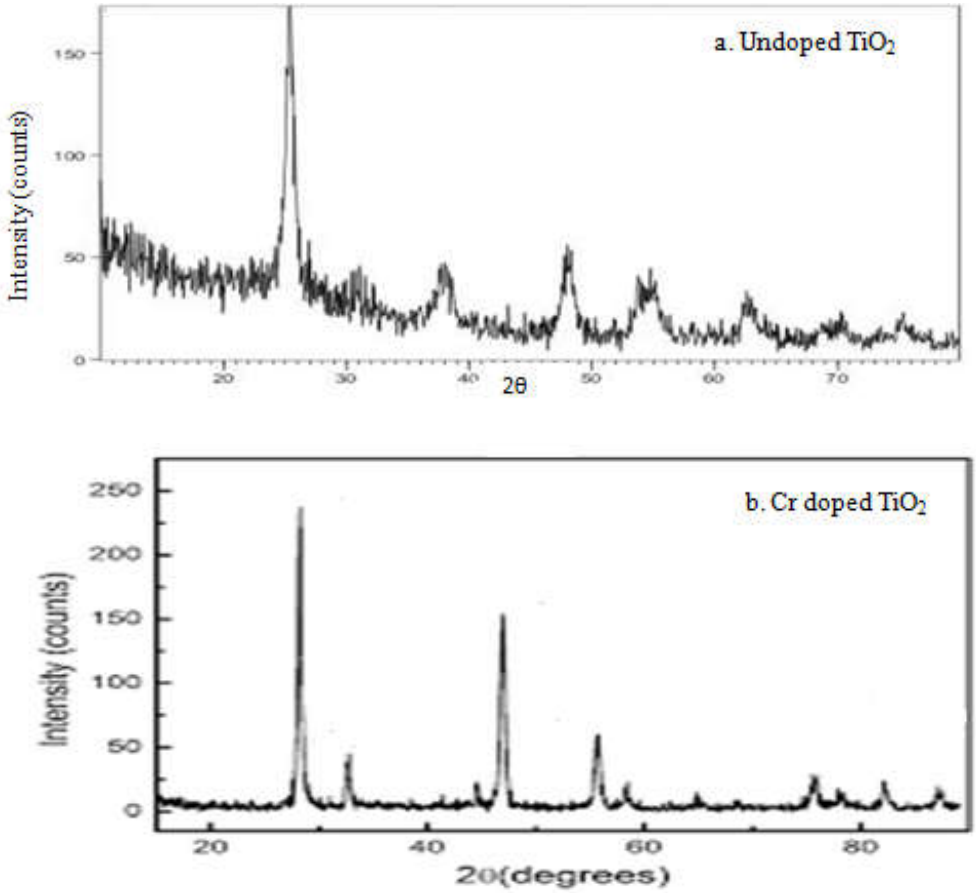


**Fig. 4. X-ray diffractogram of undoped and Cr doped $TiO_2$**

transition to these levels and resulting in narrowing of $TiO_2$ band gap (Hayat Khan and Imran Khan Swati, 2016).

**Surface area measurements (BET)**

The surface area of undoped $TiO_2$ is found to 55 $m^2/g$. It is generally observed that the surface areas of the doped samples slightly increased from those of the undoped samples. However, the difference in the surface areas of each sample is almost negligible. Hence, the differences in the photocatalytic efficiencies of these undoped and doped samples may not be due to the small differences in the surface area but due to the other factors such as dopant nature, dopant concentration, etc.

**Scanning Electron Microscope (SEM)**

Scanning electron microscope pictures have been taken for the undoped and doped $TiO_2$ shows in fig. (3). The SEM photographs of the undoped powders particle sizes are very small and compared with those of the doped samples where larger particles have been observed.

**X-ray Diffraction (XRD)**

X-ray diffraction measurements have been taken in the range, $2\theta = 20^0 - 80^0$ for the undoped and doped ($Fe/TiO_2$ and $Cr/TiO_2$) photocatalysts. The $2\theta$ values at which major peaks appear have been found to be almost the same for both undoped and doped samples except the intensities of the peaks. It is interesting to the crystallinity has been increased as evidenced from the more intense peaks observed in the doped samples. This observation is also supported by XRD spectrum Fig. (4) where more intense and sharp peaks are observed for the doped samples.

**Conclusion**

This present study showed a very simplest technique for metal doping four atomic percentage $Fe^{3+}$ and $Cr^{3+}$ the chemical groups of the samples have been identified by FTIR spectra. The cut-off wavelengths were identified by UV-Visible (DRS) analysis and the band gap energies of the undoped and doped products are lies between 3.2 eV. The SEM image of particle size confirmed that doped and undoped morphology of the products. This observation is also supported by the XRD spectrum where more intense and sharp peaks are observed for the doped samples.

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## REFERENCES

Bak, T., Nowotny, J., Rekas, M., Sorrell, C.C. 2002. "Review article: Photo-electrochemical hydrogen generation from

water using solar energy: materials-related aspects", *International Journal of Hydrogen Energy*, 27 991–1022.

Ballyy, A.R., Korobeinikova, E.N., Schmid, P.E., Levy, F., Bussy, F. 1998. "Structural and electrical properties of Fe-doped $TiO_2$ thin films", *Journal of Physical Data: Applied Physics*, 31 1149–1154.

Bickley, R.I., Lees, J.S., Tilley, R.J.D., Palmisano, L., Schiavello, M. 1992. "Characterization of iron/titanium oxide photocatalysts: part 1 - structural and magnetic studies", *Journal of Chemical Society, Faraday Transaction*, 88 377–383.

Blasse, G., Korte, P. H. M. and Mackor, A. 1981. *Journal of Inorganic Nuclear Chemistry*, 43 1499.

Cordishi, D., Burriesci, N., Alba, F.D., Petrera, M., Polizzotti, G., Schiavello, M. 1985. "Structural characterization of Fe/Ti oxide photocatalysts by X-ray, ESR, and Mossbauer methods", *Journal of Solid State Chemistry*, 56 182–190.

Dhanalakshmi, K.B., Anandan, S., Madhavan, J., Maruthamuthu, P. 2008. Photocatalytic degradation of phenol over $TiO_2$ powder: The influence of peroxomonosulphate and peroxodisulphate on the reaction rate, *Solar Energy Materials and Solar Cells*, 92 457-463.

Fujishima, A. Honda, K. 1972. "Electrochemical photolysis of water at a semiconductor electrode", *Nature*, 238 37–40.

Ganesh, I., Gupta, A.K., Kumar, P.P., Sekhar, P.S.C., Radha, K. Padmanabham, G. and Sundararajan, G. 2012. "Preparation and characterization of Co-doped $TiO_2$ materials for solar light induced current and photocatalytic applications", *Material Chemical Physics*, in press.

Ganesh, I., Gupta, A.K., Kumar, P.P., Sekhar, P.S.C., Radha, K., Padmanabham, G. and Sundararajan, G. 2012. "Preparation and characterization of Ni-doped $TiO_2$ materials for photocurrent and photocatalytic applications", *Science World journal*, in press

Hayat Khan and Imran Khan Swati, 2016.$Fe^{3+}$-doped Anatase $TiO_2$ with d–d Transition, Oxygen Vacancies and $Ti^{3+}$ Centers: Synthesis, Characterization, UV–vis Photocatalytic and Mechanistic Studies, *Industrial and Eingineering Chemistry Reserch*, *55* (23) 6619–6633.

Hu, W.B., Li, L.P., Li, G.S., Tang, C.L., Sun, L. 2009. High-quality brookite $TiO_2$ flowers: synthesis, characterization, and dielectric performance. *Crystal Growth Des*, (9) 3676–3682.

Ibram Ganesh, Polkampally P. Kumar, Abhishek K. Gupta, Panakati S.C. Sekhar, Kalathur Radha, Gadhe Padmanabham, Govindan Sundararajan. 2012**.** Preparation and characterization of Fe-doped $TiO_2$ powders for solar light response and photocatalytic applications. *Processing and Application of Ceramics,* 6 (1) 21–36.

Jakani, M., Campet, G., Claverie, J., Fichou, D., Pouliquen, J. and Kossanyi, J. 1985. *Journal of Solid State Chemistry*, 56.

Kheamrutai Thamaphat, Pichet Limsuwan and Boonlaer Ngotawornchai, 2008. Phase Characterization of $TiO_2$ Powder by XRD and TEM., *Kasetsart Journal of Natural Science,* (42) 357 – 361.

Kumari, S., Chaudhary, Y.S., Agnihotry, S.A., Tripathi, C., Vermac, A., Chauhan, D., Shrivastav, R., Dass, S. and Satsangia, V.R. "A photoelectrochemical study of nano-structured Cd-doped titanium oxide", *International Journal of Hydrogen Energy*, 32 **(2007)** 1299–1302.

Lin, Y.J., Chang, Y.H., Yang, W.D. Tsai, B.S. 2006. "Synthesis and characterization of ilmenite $NiTiO_3$ and $CoTiO_3$ prepared by a modified Pechini method", *Journal of Nano-Crystal Solids*, 352 789–794.

Litter, M.I. Navio, J.A. 1996. "Photocatalytic properties of iron-doped titania semiconductors", *Journal of Photochemistry Photobiology A Chemistry*, 98 **(**3) **(1996)** 171–181.

Liu, X.H., He, X.B., Fu, Y.B. 2008. Effects of doping cobalt on the structures and performances of $TiO_2$ photocatalyst, *Acta Chimica Sinica,* 66 1725–1730.

Mori, K., Miyamoto, A. and Murakami, Y. 1985. Catalytic reactions on well-characterized vanadium oxide catalysts. 4. Oxidation of butane, *Journal of Physical Chemistry,* 89 (20) 4265-4269.

Navio, J.A. Macias, M., Gonzalez-Catalan, M., Justo, A. 1992. "Bulk and surface characterization of powder iron doped titania photocatalysts", *Journal of Material Science*, 27 3036–3042.

Prabu, K.M. Anbarasan, P. M. 2014. Preparation and characterization of silver, magnesium and Bismuth doped titanium dioxide nanoparticles for solar cell applications, *International journal of science and research (IJSR)*, 3 (9).

Ramakrishna, G., Ghosh, H.N. 2003. Optical and photochemical properties of sodium dodecylbenzene sulfonate (DBS) capped $TiO_2$ nanoparticles dispersed in non aqueous solvents. *Langmuir*, 19 505–508.

Shan, G.B., Demopoulos, G.P. 2010. The synthesis of aqueous dispersible anatase $TiO_2$ nanoplatelets. *Nanotechnology*, 21 1–9.

Sugimoto, T., Zhou, X., Muramatsu, A. 2003. Synthesis of uniform anatase $TiO_2$ nanoparticles by gel–sol method formation process and size control. *Journal of Colloid Interface Science,* 259 43–52.

Tsodikov, M.V., Bukhtenko, O.V., Ellert, O.G., Shcherbakov, V.M. Kochubey, D.I. 1995. "Low-temperature formation mechanism of double oxides Fex Zr(Ti)1–075x$O_2$–δ prepared from alkoxides and acetyl acetonates", *Journal of Material Science*, 30 (4) 1087–1094.

Wang, Y., Cheng, H., Hao, Y., Ma, Y. Li, W., Cai, S. 1999. "Preparation, characterization and photoelectrochemical behaviors of Fe (III)-doped $TiO_2$ nanoparticles", *Journal of Material Science*, 34 3721–3729.

Yan-Hua Peng, Gui-Fang Huang, Wei-Qing Huang., 2012. Visible-light absorption and photocatalytic activity of Cr-doped $TiO_2$ nanocrystal films. *International journal of Advanced powder Technology*, 23(1) 8-12.

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