# A Literature Review on: Synthesis Approaches of Metal doped Titanium Dioxide

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**Abstract:** Titanium dioxide (TiO<sub>2</sub>) nanoparticles are synthesized using various approaches of synthesis. Various synthesis approaches are subsequently compared in terms of their morphology and structural properties like crystallite size, surface area, particle size and phase. Titanium dioxide nanoparticles have unique properties such as optical, electrical, mechanical, physical, chemical, photo catalytic and electronic. The paper presents the various methods of synthesis of pure titanium dioxide and with dopant like alkali metals, alkaline earth metals, transition metals, inner transition metals and codoped materials and its applications.

Keywords: Titanium dioxide, Nanoparticles, Synthesis, Transition metals.

# I. Introduction:

Titanium is the world's fourth abundant metal and the ninth abundant elements. This new element was discovered by the Reverend William Gregor in 1791 in ilmenite. It was rediscovered by the German chemist Heinrich Klaporth in rutile ore. He named it as Titans means mythologically the first son of the goddess Ge i.e.earth<sup>1</sup>.Primarily, it occurs in ilmenite,rutile, anatase,brookite and perovskite.

Titanium dioxide (TiO<sub>2</sub>) is one of the most important compounds in the field of the nanotechnology due to its non-toxicity, low cost, photocatalytic activity and photocatalytic activity<sup>2,3</sup>.TiO<sub>2</sub> exist in three polymorphs anatase, brookite and rutile<sup>4</sup>.Rutile is thermodynamically stable while the anatase and brookite are metastable, transforms to rutile by calcination<sup>4</sup>. Pure TiO<sub>2</sub>shows low utilization of solar energy because of wide band gap(as shown in figure-1) and low quantum yield since electron-hole pairs combines fast<sup>5</sup>.Some strategies were developed to improve the efficiency of the TiO<sub>2</sub>. Doping with metals<sup>6,7,8,97,10,11</sup>, non-metals<sup>12,13,14,15,16</sup>, depositing with noble metals<sup>17,18</sup> and combining with semiconductors<sup>19,20</sup> improves the efficiency of TiO<sub>2</sub>.



Figure-1: Comparison of band gap between the pure and doped TiO<sub>2</sub>.

Modified TiO<sub>2</sub> is widely used as skin protective compound insunscreen<sup>21</sup>, hydrogen production<sup>22,23</sup>, water splitting<sup>24</sup>, waste water treatment<sup>2,25</sup>, waterand air purification<sup>26,23</sup>, UV protection<sup>21</sup>, self-cleaning surfaces<sup>23</sup>, photo electrochemical conversion<sup>23</sup>, sterilization<sup>23</sup>, antibacterial agent<sup>26</sup>.



Figure-2: Applications of pure and doped TiO<sub>2</sub>.

In this review, we focus on the research work that has been done on metal doped  $TiO_2$ . This article will be helpful for the research scholars who have keen interest in the field of  $TiO_2$ .

# 1. Alkali metal doped

Bessekhouad and coworkers<sup>6</sup>prepared Alkali(Li, Na, K) doped TiO<sub>2</sub> nanoparticles by sol-gel route and impregnation technology. The study revealed thatthe crystallinity of the catalysts is mostly dependent on both the nature and the concentration of alkaline. The greatest crystallinity is gained for Li-doped TiO2 and is lowermost for K-dopedTiO<sub>2</sub>. For photocatalytic study, organic pollutants such as Malachite green oxalate, 4-hydroxybenzoic acid and benzamide were used. For a given alkaline concentration, the catalysts synthesised by the impregnation method were more efficient than those by sol-gel route. From

these results, they concluded that in the small concentrations, alkaline improves  $TiO_2$  efficiency. They found that the sodium can activate  $TiO_2$ .

Chen and coworkers<sup>27</sup>synthesized K<sup>+</sup> doped TiO<sub>2</sub>by sol gel method from KOH and titanium isopropoxide. From the study, it was found that doped TiO<sub>2</sub> was more photoactive than the undopedTiO<sub>2</sub>. K<sup>+</sup> doping with TiO<sub>2</sub>decreases the size of the TiO<sub>2</sub> crystals, increases the surface area and the temperature at which anatase changes into the rutile phase. The catalyst was used for the photodegradation of Everdirect Supra Blue BRL dyes (BRL). The optimal K<sup>+</sup>amount was 4.6% while the calcination temperature was 973 Kfor the photoactivity. The most effective pH for the BRL was 7.2. The photocatalytic reaction rate has found to be be with the increase of the catalyst dosage to the power of 0.72 and the optimal dosage of K<sup>+</sup> catalyst is around 1.5 g/l.

## 2. Alkaline earth metal doped:

Salim and coworkers<sup>28</sup> synthesized calcium, strontium or barium ions doped TiO<sub>2</sub> (anatase)photocatalyst powders by sol gel method.Greater than 15 mol% alkaline earth ions compositions resulted in largely amorphous materials. As the concentration of alkaline earth ions increases, the residual anatase showed decrease in the crystallite sizes and increase in the crystallographic cell volumes, while the BET surface areas of the materials increases at higher levels of additive. The band gaps of the materials increased with increasing of the Ca<sup>2+</sup> content, due to the decreasing particle sizes. During the synthesis, except rutile (v1% w.r.t. anatase), no other crystalline phase was observed. Oxalic acid was used for the determination of the relative effects of the additives on the photocatalytic activities.From this study, it was found that the titania containing 20 mol% alkaline earth ions showed approximately double the photocatalytic activity.

## 3. Transition Metal doped:

Ghasemi and coworkers<sup>7</sup> has synthesized nanocrystalline transition metal (TM) doped TiO2 by using solgel method. They use 2-hydroxylethylammonium formate as a ionic liquid as a solvent media. They doped transition metals such as Cr, Mn, Fe, Co, Ni, Cu, and Zn with TiO<sub>2</sub>. The findings revealed that doped nanoparticles have reduced crystalline size as well as higher surface area than pure TiO<sub>2</sub>. They found a noteworthy absorption shift into the visible region due to dopant ions in the TiO<sub>2</sub> structure. The TM doped TiO<sub>2</sub> nanoparticles exhibited higher photocatalytic activity than pure TiO<sub>2</sub> for the degradation of Acid Blue-92(AB92) in water. The increase in activity may be due to higher efficiency for the electron–hole generation and lower the electron–hole recombination rate.

Rauf and coworkers<sup>29</sup> has studied the degradation of azo dyes using transition metal (Cr, Cu, Fe, Mn, Zn, V, Ag and W) doped TiO<sub>2</sub> as photocatalysts in aqueous solutions. These dopants reduce the recombination of e–cb and h+vb and decrease the band gap or create intra-band gap states that result in more light absorption. Likewise, these dopants can alter the surface properties such as surface acidity and surface area, of the TiO<sub>2</sub> catalyst. Thus, by using the visible light, the photocatalysis on modified TiO<sub>2</sub>

can be promoted. They study the effect of pH, catalyst concentration, substrate concentration and the nature of the doping substances, on the degradation of dyes. Transition metal doped  $TiO_2$  has found to be very effective for the photodegradation of azo dyes. The photocatalytic processes became more efficient through the formation of intermediates such as aromatic amines, phenolic compounds and several organic acids result in enhanced dye degradation.

# 3.1 Silver (Ag)doped

Sokemon and coworkers<sup>17</sup> synthesized silver-loaded TiO2.This catalyst was studied for the photocatalytic degradation of organic dyes. The dyes such as methyl violet, a cationic dye; Cibacron Blue FMR, a reactive dye; and Maxilon Red GRL, a mono azo basic dye were used for the degradation study. They found that the undoped TiO<sub>2</sub> degraded about 63% of methyl violet within 4 min while the Ag-loaded TiO<sub>2</sub> catalyst degradated the same to 95% within the same time period.Finally, they concluded that the Ag-loading dramatically reduced the degradation time.

Lee and coworkers<sup>18</sup>synthesized the Ag-TiO<sub>2</sub> particles by sol–gel process involving a reduction agent. The sol synthesized was transparent and stable for several months. The prepared Ag-TiO<sub>2</sub> particles were mostly an anatase structure, regardless of the AgNO<sub>3</sub> content. All the particles had a crystallite sizes in between 5 and 6nm. They found that the addition of AgNO<sub>3</sub> did not affect the crystallite size of the particles. It was cconfirmed that the calcination improves the crystallinity of the particles. With the increase of calcination temperature, the amorphous TiO<sub>2</sub> changing into the anatase phase and then the anatase phase changing into the rutile phase. In addition, they colclude that the presence of Ag in TiO<sub>2</sub> resulted in higher photodegradation of p-nitrophenol and the photocatalytic activity of TiO<sub>2</sub>–Ag increased with increasing AgNO<sub>3</sub> content.

# 3.2 Iron (Fe) doped

Marami and his coworkers<sup>30</sup> prepared Fe doped TiO<sub>2</sub> by the simple sol–gel synthesis method. The XRD patterns study revealed the coexistence of rutile and anatase phases and the structure was determined to be tetragonal for both undoped and doped TiO<sub>2</sub>. The mixed phase ratio of the rutile-to-anatase was 29:71. The particle size of about 18 nm for 4 mol.% Fe-doped TiO<sub>2</sub>. The the XRD results, it was found that the increase of Fe impurity decreases the crystallite size. The UV- DRS dataexhibited a red shift, because of the reduction of the band gap produced by the increase of Fe content. The optimal bandgap was found for 4 mol.% Fe-doped TiO<sub>2</sub> at about 2.6 eV.From their study, it was concluded that the Fe3+ ions increase the photocatalytic activity by the separating the photogenerated charges, affecting the material efficiency as a photocatalyst for solar energy conversion.

Wang<sup>31</sup> and his colleagueswere synthesized novel  $M(OH)x/TiO_2$  nanoparticles by the modified wet precipitation process at low temperature, where M(OH)x represents ferric(Fe<sup>3+</sup>) or cupric(Cu<sup>2+</sup>) hydroxide. Methyl orange (MO) as a model of organic pollutants was used to study the photocatalytic activity. XRD, UV–vis DRS, TGA, and FT-IR characterization showed that these nanoparticles hasa surface that enriched with hydroxyls and coordinated water. These composites showed a strong

photocatalytic activity in the degradation of methyl orange in aqueous solution. The photocatalytic activity of 0.05-M(OH)x/TiO<sub>2</sub> was increased by about fivefolds as compared to the undoped TiO<sub>2</sub>. From this study, it was revealed that the new photocatalysts has outstanding photocatalytic activity with the pH range from about 3 to 7. Simple preparation method and excellent photochemical stability were the most important features of this catalyst. From this study, it was concluded that the improved effect of M(OH)x/TiO<sub>2</sub> that promotes the charge separation.

Zhu and coworkers<sup>32</sup> were prepared iron-doped TiO2 photocatalysts by the combination of sol–gel process with hydrothermal treatment. This method produced anovel photocatalysts that have high surface areas, mesoporous structure, and small crystal sizes. Moreover, this catalyst also have a large amount of surface adsorbed water and hydroxyl groups that contributes to their high photocatalytic activity. From this study, it revealed that there was a decrease in the Fe<sup>3+</sup> doping content from the surface to the core. This dopant distribution may be in favor of the interfacial transfer charge reactions. Fe<sup>3+</sup> can assist the separation of the photogenerated electrons and holes by trapping them tempoararoly. Doped photocatalysts absorb and utilize the visible light for the photocatlytic degradation of the yellow XRG.

#### 3.3 Cobalt(Co) doped

Bouras and coworkers<sup>33</sup> has synthesized the thin films of pure or doped nanocrystalline  $TiO_2$  on glass slides by using a sol–gel procedure. The Triton X-100 was used as surfactant that acts as template of the nanostructure. Fe<sup>3+</sup>, Cr<sup>3+</sup> and Co<sup>2+</sup> were used as dopants with a concentration from low to high levels. The photocatalytic efficiency of undoped or doped  $TiO^2$  was studied for the degradation of Basic Blue-41. In this work, they found that the pure nanocrystalline  $TiO_2$  is a better photocatalyst than doped  $TiO_2$ .

Chekuri and colleagues<sup>34</sup>has synthesized 0.5 wt. %  $Co^{2+}$  doped TiO<sub>2</sub> by sol-gel method and used 1,4-Butane sultone anionic Gemini surfactant. From the results it was found that the surfactant controlled the grain morphology, theparticle sizes and the specific surface area. Thesuperior activity of the  $Co^{2+}$ -TiO<sub>2</sub> (withsurfactant) for Acid Red dye degradation efficiency was attributed due to decrease in band gap,small particle sizeand then enhanced specific surface area. In addition, the catalyst showed astronger absorption in the visible region and shift in the band gap transition was observed at 400nm- 800 nm. This shift was related to the doping of cobalt into TiO<sub>2</sub>. The photocatalyticdegradation of Acid Red, model azo-dye pollutant has been studied in detail. From the XRDstudies, all the  $Co^{2+}$ -TiO<sub>2</sub> (with surfactant) catalysts synthesized were reported in anatase phase.The crystallite size was obtained ranging from 8nm-14 nm. From XPS chemical analysis it hasbeen confirmed that the presence of cobalt was present in the catalyst as  $Co^{2+}$ . SEM micrographshave indicated change in morphology. Due to doping of cobalt into TiO<sub>2</sub> lattice morphologicalchange of the TiO<sub>2</sub> particles has been observed with decrease in particle size for the dopedcatalyst in presence of catalyst. From TEM analysis of the catalyst were reported with muchreduction in particle size of 8-12 nm. This was due to encapsulation of cobalt doped TiO<sub>2</sub> by the surfactant which restricted the further growth of particle resulting in formation of particleswith much

reduction. FT-IR studies revealed that cobalt was doped substitutionally into the  $TiO_2matrix$ . The optimum conditions for the degradation of acid red dye solution with catalyst werefound at 0.5 wt. % dopant concentration with pH-4, 0.1g catalyst dosage and 5 mg L-1 as initialdye concentration. The observed rate at optimum conditions for the degradation of Acid Red wasfound to be 13.81 mg L-1min-1. The synthesized catalyst was proved to be effective wheredegradation was completed within 30 min. Hence the catalyst  $Co^{2+}-TiO_2$  prepared in presence of gemini surfactant had exhibited the highest photocatalytic activity.

Hamadanian and coworkers<sup>35</sup> were synthesized undoped and Co doped TiO<sub>2</sub> nanoparticles by solgel method with sonication. Form their study, it was concluded that the doping of Co in the TiO<sub>2</sub> decreases the grain size. This doping shows the red shift (the absorption to higher wavelength) and lowers the surface area. The photocatalytic activity of these catalyst was studied on the methyl orange under UV and visible irradiation. In their study, it was revealed that the activity of the catalyst was higher in the presence of the undoped TiO<sub>2</sub> than the cobalt doped TiO<sub>2</sub>. Among the doped samples, the 1.0% Co doped TiO<sub>2</sub> catalyst exhibited the highest photocatalytic activity under UV irradiation while the presence of 0.5% of cobalt doped TiO<sub>2</sub> exhibited the highest activity under visible irradiation.

Mugundan and coworkers<sup>36</sup>synthesized undoped and 4, 8, 12 and 16 % cobalt doped  $TiO_2$  nanoparticles by sol–gel method at room temperature. In their study it was revealed that theall doped samples show increased particle size as compared to undoped catalyst. The band gap energies values of the  $TiO_2$  and Co doped  $TiO_2$ was in between 3.58 and 3.93 eV. The catalyst also shows the photoluminescence emission spectra that shows the creation of new luminescent centers.

# 3.4 Copper (Cu) doped

Wong and coworkers<sup>37</sup>synthesized Cu-doped TiO<sub>2</sub> by photo-deposition and sol–gel methods. These catalystswere used to study the photocatalytic activities of the organic dye, Orange-II. From this study it was revealed that the Cu-doped TiO<sub>2</sub> catalystsprepared by the photo-deposition method showed enhanced photocatalytic activity than the catalysts synthesized by the sol–gel method. It was revealed that the 1% Cu doped TiO<sub>2</sub> showed the best performance. The catalyst has remove the color completely. By using this catalyst, about 99% of the total organic carbon (TOC) was removed after 150-min of reaction. It was found that, more than 1% amount of Cu doped with the TiO<sub>2</sub> by the photo-deposition method, there was a decreased in the photocatalytic activities of the catalyst.

Yoong and coworkers<sup>22</sup> synthesized a 10% Cu-Glycerol complex  $TiO_2$  (10CuGT) photocatalyst by the complex-precipitation method. This catalyst showed better activity than the other wet impregnation catalyst. SEM analysis predicts that there were a relatively uniform dispersion of CuO on TiO<sub>2</sub>. This uniform dispersion of the dopant confirms the fast charge transfer from TiO<sub>2</sub> to CuO.

Khairy and coworkers<sup>38</sup> investigated the photocatalytic activities Cu and Zn doped TiO<sub>2</sub> nanoparticles for the chemical oxygen demand (COD) and degradation of methyl orange. The XRD results of these nanoparticles has confirmed the formation of the anatase phase for the TiO<sub>2</sub> nanoparticles. Their crystallite sizes were in the range of 9–21 nm. The growth of the TiO<sub>2</sub> anatase phase was due to the small crystallite size and doping ions (Cu and Zn) that inhibited any phase transformation. From the optical study, they found that the doping ions lead to an increase in the absorption edge wavelength, and a decrease in the band gap energy of TiO<sub>2</sub> nanoparticles. The doped TiO<sub>2</sub> nanoparticles in general showed higher photocatalytic activities than the pure ones. Based on measured chemical oxygen demand (COD) values, they conclude that the Cu doped TiO<sub>2</sub> nanoparticles showed the best photocatalytic activity. The catalytic degradation rate under both UV and visible radiation decreases according was in the order of: Cu/TiO<sub>2</sub>> Zn/TiO<sub>2</sub>> TiO<sub>2</sub> pure. The improved photocatalytic activity under light irradiation is due to incorporation of doping metal ions that diminished the electron-hole recombination. The kinetics of photo-degradation of methyl orange followed first order reaction. The Cu/TiO<sub>2</sub> showed the highest rate constant and the highest efficiency in chemical oxygen demand (COD)

## 3.5 Nickel (Ni) doped

Ganesh and coworkers<sup>39</sup>preparedNi (Ni = 0.1 to 10%)-doped TiO<sub>2</sub>nanomaterialas well as thin films by a coprecipitation and sol-gel dip coating method, respectively. TheTiO<sub>2</sub> nanomaterial prepared from TiCl<sub>4</sub> by a coprecipitation method exists in the form of crystal pure rutile phase, while the Ni doped TiO<sub>2</sub> powders up to 6% was exist mainly in anatase phase. It was found that 0.1% Ni is enough to transform TiO<sub>2</sub> from rutile to anatase phase and to enhance its BET surface area. The dopant Ni reduces its bandgap energy significantly and absorb energy from a major portion of visible light. The 9 % Ni-doped TiO<sub>2</sub>nanomaterial show maximum absorption of the visible light at a wavelength 448 nm, while the 10 % doping shows maximum absorption ata wavelength 840 nm. Among all Ni-doped TiO<sub>2</sub>nanomaterials, 0.1% Ni doped TiO<sub>2</sub>shows the highest photocurrent and the 0.5% Ni doped TiO<sub>2</sub>shows the highest photocatalytic activity. The photocatalytic activities of methylene blue (MB)were studied under simulated solar light. The characterization study revealed that Ni as dopant stabilizes TiO<sub>2</sub> in the form of anatase phase and lowers its bandgap energy. The photocurrent ability as well as the photocatalytic activity fiO<sub>2</sub> have been improved with doping of Ni in TiO<sub>2</sub>.Langmuir-Hinshelwood first-order rate constant relationship was followed by the Ni-doped TiO<sub>2</sub> powders in the photocatalytic degradation reactions.

Hermawan and Worker<sup>40</sup>has prepared Ni(II) doped TiO<sub>2</sub> nanomaterial by sol-gel method. The concentration of Ni(II) plays a noteworthy role in thespectra absorption, crystal structure, particle size and band edge absorption. From their study it was concluded that the addition of 5% Ni/TiO<sub>2</sub> increases the absorbance and the particle size, while decreases the bandgap energy.

Manzoor and coworkers<sup>10</sup> synthesized the undoped and Ni doped TiO<sub>2</sub> nanoparticles by sol-gel method. Titanium butoxide and nickel nitrate were used as onprecursors and methanol as a solvent. The Ni doped TiO<sub>2</sub> samples with doping concentration at 5, 10, 15, and 20% were prepared. The XRD study of the

undoped and doped material shows tetragonal system with anatase phase. In this research it was found that the particle size was decreased with increasing amount of Ni in TiO2 The blue shift was found with small contents of Ni–TiO<sub>2</sub>while the red shift was found higher contents of Ni–TiO2, that enhanced the bandgap with doping. Ni-doped TiO<sub>2</sub> is a magnetic semiconductor. Hence, it has many applications in spintronics, electron transporting layer, oxygen sensor and UV light absorber in photovoltaics.

## 3.6 Chromium (Cr) doped:

Inturi and coworkers<sup>41</sup>observed that the flame spray pyrolysis (FSP) Cr-TiO<sub>2</sub> has superior activity when compared with the other given synthesis methods (Sol-Gel and Co-Precipitation). The photocatalytic activity of the synthesized catalysts was studied for photocatalytic degradation of 4- chlorophenol under visible light (400–800 nm) conditions. It was found that the flame spray pyrolysis Cr-TiO<sub>2</sub> has superior photocatalytic activity to other synthesis methods. The sol-gel and co-precipitation produce the anatase phase only of the material. In their study, it was found that the higher concentration of the Cr (IV) in the materials that is a noteworthy factor for the improving in the photocatalytic activity of the materials. They observed the development of the photocatalytic activity, withan addition of the Si, as a support. It also improves the surface area and structural stability.

Zhu and co-workers<sup>42</sup> has synthesized the  $Cr^{3+}$ -dopedtitanium dioxide (anatase) photocatalysts by combine methods of sol–gel process with hydrothermal treatment. The photocatalytic activity study of the Cr doped TiO<sub>2</sub> was performed on an aqueous solution of the azoic dye XRG. This study has done both under UVand visible light irradiation. In their study they found that the Cr-TiO2 shows a good ability for absorbing the visible light for the degradation of the XRG. Chromium ions doping improves the photocatalytic activity of the catalyst under both UV light irradiation and visible light.

# 4. Inner Transition doped

# Lanthanide (La<sup>3+</sup>) doped:

EI-Bahy and his colleagues<sup>43</sup>were synthesized Lanthanide ionsdoped TiO2 nanoparticles by sol-gel method. They used La<sup>3+</sup>, Nd<sup>3+</sup>, Sm<sup>3+</sup>, Eu<sup>3+</sup>, Gd<sup>3+</sup> and Yb<sup>3+</sup> as the dopants. Direct Blue dye (DB53) was used to study the photocatalytic activity. The XRD data showed a characteristic anatase phase but the lanthanides phase was not detected on Lanthanide ions/TiO<sub>2</sub>. The results analysis of this research shown that the Gd3+/TiO<sub>2</sub> has lowest particle size, bandgap, highest surface area and pore volume (Vp) too. Lanthanide ions improve the photocatalytic activity to some extent as compared with undoped TiO2. It was found that, Gd3+/TiO<sub>2</sub>was the most active photocatalyst among all the doped TiO<sub>2</sub>. The photocatalytic degradation occur at the optimum conditions. The illumination time was 40min, pH~4, photocatalyst loading-0.3 g/L and 100ppm DB53. This photocatalyst has 100% dye removal efficiency.

Liang and colleagues<sup>44</sup> prepared Undoped  $TiO_2$  and erbium ion-doped  $TiO_2$  ( $Er^{3+}-TiO_2$ ) photocatalysts by the sol–gelmethod. From the XRD data it was found that the doping of the erbium ion could increase the thermal stability of  $TiO_2$  and inhibit the growth of the crystallite size. DRS results

shown that the optical absorption slightly shifted to red direction due to erbium ion. In aqueous suspension of undoped TiO<sub>2</sub> or  $Er^{3+}$  doped TiO<sub>2</sub> catalysts; the adsorption isotherm, oxidation and mineralization of orange I were studied. $Er^{3+}$ -TiO<sub>2</sub> photocatalyst had advanced adsorption equilibrium constants and improved adsorption capacitythan undoped TiO<sub>2</sub>. The  $Er^{3+}$ -TiO<sub>2</sub> catalyst adsorption equilibrium constants (Ka) were approximately double those of pure TiO<sub>2</sub>. The  $Er^{3+}$  doped TiO<sub>2</sub> catalyst 's overall adsorption efficiency (Qmax) was greater than that of pure TiO<sub>2</sub>. The 2.0 percent  $Er^{3+}$ doped TiO<sub>2</sub> catalyst gained the highest Qmax and Ka values among the catalysts  $Er^{3+}$ -TiO<sub>2</sub>. The results indicated that the degradation and mineralisation of orange I with the  $Er^{3+}$ -TiO<sub>2</sub> catalyst was more effective than with pure TiO<sub>2</sub> under both UV and visible light. The highest degradation rate was achieved by optimal dosage of erbium ion at 1.5 per cent. The transitions of 4f electrons of  $Er^{3+}$  and the red shift of the optical absorption edge of TiO<sub>2</sub> by  $Er^{3+}$  doping were useful to enhance photocatalyticactivity under visible light.

#### 5. Codoped

Devi and coworkers<sup>45</sup> synthesized anatase TiO<sub>2</sub> doped with divalent transition metal ions like  $Mn^{2+}$ ,  $Ni^{2+}$  and  $Zn^{2+}$ . Photocatalytic activity of these catalyst has been studied in the degradation of Aniline Blue under UV/solar light. In their study, they found that the dopant  $Ni^{2+}$  and  $Zn^{2+}$  metal ions stabilize the anatase phase while  $Mn^{2+}$  promotes phase transformation to rutile as a result of formation of surface oxygen vacancies. In this study, they found the enhanced activity of  $Mn^{2+}(0.06 \text{ at.}\%)$ –TiO2 both under UV/solar light because of: (I) anatase and rutile in their bi-crystalline framework shows synergistic effect; (II) smaller crystallite size that enable the effective interparticle electron transfer; (III) half-filled electronic structure of  $Mn^{2+}$ , that assists as shallow trap for the charge carriers.

Kiriakidis and coworkers<sup>46</sup> synthesized Mn, Co and Mn-Co doped TiO<sub>2</sub>ternary and quaternary semiconducting materials by the co-precipitation method, with particle sizes in the range between 35-40 nm.These catalysts were used in the degradation of methylene blue under visible light irradiation. In their study, it was found that these materials show a red shift. Depending on the type of the dopant and concentration, these materialshows absorption in the visible region. These materials found to be more effective photocatalysts in visible light.In the case of Co and Mn/Co dopants, they found an extra subband gap.Under visible light, the photocatalytic efficiencies of doped catalyst were found to be significantly higher. They concluded that these doped catalystswere useful for the degradation of organic pollutants and industrial wastewater treatment than the conventional undoped TiO<sub>2</sub>.

Kudo and coworkers<sup>47</sup> has studied the effects of doping of metal cations into wide band gap semiconductor photocatalysts. They study the effect of doping effect on the morphology, visible light response, and photocatalytic performance of the catalysts. Doping of lanthanide and alkaline earth ions has improved the activity of a NaTaO<sub>3</sub> photocatalyst for water splitting. Lanthanum was found to be the most effective dopant. However, metal cation doping in ZnS, TiO<sub>2</sub>, and SrTiO<sub>3</sub>provided visible light responses for hydrogen(H<sub>2</sub>) or oxygen(O<sub>2</sub>) evolution from aqueous solutions containing of sacrificial cations, resulting in the improvement of visible light response for photocatalytic reactions.

reagents. Co-doping was effective to compensate charge unbalance brought by doping of transition metal

#### **Future Scope:**

This literature review will be benificial for research scholars those who are interseted in the filed of systemes and metal doped titanium dioxide.

#### Acknowledgement:

We are very much thankful to M.G. V's Arts, Science and Commerce College, Surgana, Dist. Nashik, Maharashtra for providing facilities. I would also thanks to Principal of our college, for his constant guidance and extensive support to encourage for this work.

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