

PREFACE

Among the transition metal (TM) oxides, titanium dioxide (TiO_2) attracts the attention of the researchers due to its stability, non-toxicity, low cost and environmental friendly nature. It is well known that TiO_2 has three natural polymorphs: Brookite (Orthorhombic structure, Pbca), anatase (Tetragonal, $\text{I4}_1/\text{amd}$) and rutile (Tetragonal, $\text{P4}_2/\text{mmn}$). The anatase and brookite phases are thermally metastable, however the rutile is the most stable phase [Ricci et al. (2013) and Bharati et al. (2017)]. Previous reports show that the structural properties of TiO_2 are modified considerably by varying synthesis conditions, precursors, dopants and irradiating with energetic ion beam etc. [Rath et al. (2009)a, Xia et al. (2012) and Bharati et al. (2018)a]. Ishikawa et al. (2006) have observed the suppression of anatase phase in TiO_2 thin films after irradiating with 200 MeV Au ions. On the other hand, Thakur et al. (2011)a, show phase transition from anatase to mixed brookite and rutile phase after irradiating with 200 MeV Ag ions. 50 keV Ar ions could amorphise the nanorods of TiO_2 [Saini et al. (2016)]. Formerly, we have shown amorphisation of Co doped TiO_2 thin films after irradiating with swift heavy ions [Mohanty et al. (2014)b]. Earlier, anatase-to-rutile phase transformation (ART) has been reported due to particle size, calcination temperature and dopant concentrations. It has been established that the anatase phase of TiO_2 becomes most stable when the size of the particle is less than 15 nm [Zhang et al. (1998) and Lu et al. (2003)]. Wetchakun et al. (2012), observe ART phase transformation by varying calcination temperature in the range 500 to 600 °C. However, Choudhury et al. (2013)a, show anatase-rutile mixed phase at 700 °C and rutile phase at 950 °C. There are number of reports on phase transformation of TiO_2 by altering the dopant. It is revealed that while Sn doped TiO_2 exhibits rutile phase [Fu et al. (2014)], Mn doped TiO_2

nanoparticles achieve anatase to rutile transformation at calcination temperature ~ 700 to 800 $^{\circ}\text{C}$ [Chauhan et al. (2012)]. Ni doped TiO_2 calcined at 550 $^{\circ}\text{C}$ hinders formation of rutile phase thereby stabilized anatase phase due to particle size less than 50 nm [Bahadur et al. (2012)]. Since the discovery of room temperature ferromagnetism (RTFM) in Co-doped TiO_2 reported by Matsumoto et al. (2001), an extensive research work has been performed on the magnetic properties of TM, such as Mn, Fe, Co and Ni doped TiO_2 [Zhang et al. (2016), Tian et al. (2008), Mohanty et al. (2012) and Sharma et al. (2011)]. Choudhury et al. (2013)b, reveal that Mn doped TiO_2 nanoparticles exhibit ferromagnetic ordering essentially due to formation of oxygen vacancies. Thakur et al. (2011)b, report transformation of paramagnetism to ferromagnetism in TiO_2 thin films after irradiating with 200 MeV Ag^{15+} ions. In our earlier report, we have also observed room temperature ferromagnetism because of doping cobalt in TiO_2 thin films before and after irradiating with 100 MeV Ag^{7+} ions [Mohanty et al. (2014)b]. In addition to rich structural transformation and unusual magnetic behavior in TiO_2 , from the past few years, photocatalytic nature of TiO_2 has also been explored by different research groups after being examined by Fujishima and Honda et al. (1972). There are reports on TiO_2 which show the effect of calcination temperature on phase transformation and photocatalysis under UV light [He et al. (2014) and Bessergenev et al. (2015)]. TiO_2 is now being widely used, because it is the most efficient photocatalyst for water purification. In current time, the non-biodegradable and persistent organic substances such as organic dyes have high carcinogenic and toxic nature [Yu et al. (2016)]. Photocatalysis is a potential technology to degrade pollutants which caused significant harm to the human health and ecosystem using only UV or visible light [Qi et al. (2014)]. Two major challenges persist in photocatalysis process; one is to suppress the recombination of

electron and hole pairs and second is to shift the absorption edge of TiO_2 from UV to visible range [Wang et al. (2014)]. To face the challenges different groups show photocatalysis behavior using B and Bi codoped TiO_2 [Bagwasi et al. (2013)], S and Fe doped TiO_2 [Niu et al. (2013)], Mn doped TiO_2 [Chauhan et al. (2012), Binas et al. (2012), Deng et al. (2011)] nanoparticles etc. It has been done under simulated visible light (1000 W halogen lamp and 300 W halide lamp) with large amount of catalyst but could not achieve 100% degradation of pollutants. Photocatalysis of transition metal oxides with cement to make the self-cleaning cement has been attracted by researchers recently. In this context, Khataee et al. (2013), explain the self-cleaning property of white Portland cement with commercial TiO_2 nanoparticles after carrying out photocatalysis by degrading C.I. Basic Red 46. It is further shown that the self-cleaning property of the sample is enhanced with increasing the amount of TiO_2 nanoparticles in cement upto 3%. Singh et al. (2018), study the photocatalytic degradation of Rhodamine 6G using ZnO nano-needles embedded in white cement under UV-light. Li et al. (2016), synthesize a new photocatalytic cement material by coating TiO_2 on EMR-cement and assessed the photocatalytic activity under UV light by degrading methyl orange. Most of the reports show photocatalytic degradation either by using UV light and/or simulated visible light. On the basis of literature, there are lot of challenges in TiO_2 regarding its structural transformation, physical properties and applications. Few of them are addition of dopants and changes in concentrations, effect of ion irradiation on structural transformation. In the present work, we have examined the structure, microstructure and magnetic properties of TiO_2 nanoparticles by doping Mn as well as examined the same by irradiating TiO_2 thin films deposited through e-beam evaporation technique using 500 keV Ar^{2+} ions of different fluences. In addition to structural modifications, we have also examined

the degradation of organic pollutants using TiO_2 , Mn doped TiO_2 and TiO_2 with cement composite under sunlight.

At the end of the thesis, we discussed the main findings of the present work and listed a few suggestions for future investigations.

List of journals and books used to bind up the thesis has been given at the end of the thesis as references.