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Study and Synthesis of Manganese Doped Tio2 Nanoparticles

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Abstract: ***Nanoparticles of un-doped, 5%, 10%, 15% Mn doped TiO2 were prepared by the sol-gel technique by adding different proportions of Manganese to the Titanium dioxide and characterized using XRD and SEM. This increase in doping proportion of Mn in the oxide material reduced the band gap to a larger extent, so this material is activated under visible light. As the doping level of Manganese increased, the material acquired the property of Ferromagnetism in room temperature. The simulation studies were carried out using DFT tool and analyzed.***

Keywords: Nanoparticles, Sol-gel, XRD, SEM, Band Gap, Ferro-Magnetism, Simulation, DFT Tool.

I.INTRODUCTION

Over the course of history, the advancement in the field of Nanotechnology is huge. A recent development in science and technology is to synthesize new and different kinds of nanoparticles (Nanowires, Nano sheets) with different methodologies. The size of these particles is of 1- 100nm. In nanotechnology, a particle is a small object that which behaves as complete unit with respect to its transport and properties. Nanoparticles play a crucial role in a wide variety of fields such as environmental detection advanced materials, pharmaceuticals, and monitoring. Nanoparticles often can display properties that differ from their bulk counter-part.

Since the research of photo catalytic water split on TiO2 electrodes was conducted in 1972 [1], the photo catalytic oxidation of aqueous and gaseous contaminants has been extensively studied. It has drawn considerable academic interest as a very attractive, non-selective, room-temperature process for the degradation of organic pollutants [2–3]. It is a process where the illumination of a semiconductor forms photo excited electrons and holes (in a vacant conduction band) that will react with contaminants adsorbed on the photo catalyst surface. TiO2 is an III-V semiconductor with wide direct-gap (3.2-3.35 eV) and exciton binding energy (60 meV) at room temperature [4]. It is an inexpensive and environmentally safe host material.

Due to its properties, the interest in TiO2 as a photo catalyst has increased, however, it has been mainly used under ultra violet (UV) irradiation. Photocatalytic reaction is initiated when a photo-excited electron is promoted from the filled valence band (VB) of a semiconductor photocatalyst (SC) to the empty conduction band (CB) as the absorbed photon energy, *hv*, equals or exceeds the band gap of the photo catalyst. The whole pair (e--h+) is generated at the surface of the photo excited photo catalyst as shown below [4-5].

Photo excitation: $SC + h\nu \rightarrow e^- + h^+$ (1)
Adsorbed oxygen: $(O2)$ ads $+e^- \rightarrow - O^{2-\bullet}$ (2)
Ionization of water: $H2O \rightarrow OH^- + H^+$ (3)
Protonation of super oxides:

$O^{2-\bullet} + H^+ \rightarrow HOO^\bullet$ (4)
$HOO^\bullet + e^- \rightarrow HO^{2-}$ (5)
$HOO^- + H^+ \rightarrow H_2O_2$ (6)
$H_2O_2 + e^- \rightarrow OH^- + OH^\bullet$ (7)
$H_2O + h^+ \rightarrow H^+ + OH^\bullet$ (8)

Since 46% of solar energy consists of visible light, it is more economical to use visible light than UV light in large scale operations. To use visible light, TiO2 however has several drawbacks including the low surface area or big particles size and an unsuitable band gap energy (E_g=3.7 eV). It was observed that doping with 3d metals reduced the E_g of semiconductors by forming inter band-gap localized levels [6]. Another technique involves modifying TiO2 with transition metals such as Fe, Cu, Co, Ni, Cr, V, Mn, Mo, Nb, W, Ru, Pt and Au . Among the transition metals, Mn is preferred due to the presence of the d-electron as the t_{2g} of manganese (Mn) is very close to the VB [7]. The incorporation of transition metals in the Titania crystal lattice may result in the formation of new energy levels between VB and CB, inducing a shift of light absorption towards the visible light region. Photo catalytic activity usually depends on the nature and the amount of doping agent [8].

II. RELATED WORK

Observation of room temperature ferromagnetism (RTFM) is reported in polycrystalline thin films of Ti1_xMnxO2 (x 5 0.10 and 0.15) synthesized by spray pyrolysis technique on fused quartz substrates. The experimental results clearly suggest partial incorporation of manganese (Mn) in titanium dioxide (TiO_2) lattice up to certain extent and rest of the Mn ions are consumed to form secondary Mn-related phase such as manganese oxide (Mn_3O_4). The observed weak ferromagnetic ordering at room temperature in the films is established to be due to incorporation of Mn in TiO_2 matrix rather than the presence of other secondary phases since none of the Mn or Ti/Mn oxide phase is ferromagnetic at room temperature [9].

Transition metal (Mn, Fe, Co,) doped TiO_2 nanoparticles were synthesized by the sol-gel method. All the prepared samples were calcined at different temperatures like 200∘C to 800∘C and characterized by X-ray diffraction (XRD) and energy dispersive X-ray (EDX) analysis. The study revealed that transition metal (TM) doped nanoparticles have smaller crystalline size and higher surface area than pure TiO_2. Dopant ions in the TiO_2 structure caused significant absorption shift into the visible region. The results of photodegradation of formaldehyde in an aqueous medium under UV light showed that photocatalytic activity of TiO_2 nanoparticles was significantly enhanced by the presence of some transition metal ions [10].

Precious metals doped anatase titanium dioxide nanoparticles are used in various applications including environmental photocatalysis and solar cells. In this work, the synthesis of Au- and Pt-doped TiO_2 nanoparticles employing sol-gel methodology. The doping procedures based on reduction by UV photo deposition. The morphology, composition, particle size and specific surface area of these synthesized nanoparticles have been characterized using several instrumental techniques namely, Scanning Electron Microscopy (SEM), Energy Dispersive X-Ray Spectroscopy (EDXS), X-Ray Diffraction (XRD), Transmission Electron Microscopy (TEM) and N_2-adsorption Brunauer–Emmett–Teller (BET) methodology. Au impregnated (2%) Nano anatase TiO_2 powder was examined in photo decolourization of Orange Gas dye environmental pollutant under visible light illumination and optimum operational conditions [11].

Nanostructures Nobel methods have unusual physicochemical properties and biological activities compared to their bulk parent materials. Thus in recent years, a number of physical, chemical and biological techniques were applied for the development of metal nanoparticles (NPs). This study aimed at developing superior quality TiO_2 based nanomaterial for photovoltaic applications, with the major contributions of this study being the following. Synthesis of Mg, Ag and Bi doped TiO_2 nanomaterial using an acid modified sol-gel technique. In this paper, we investigate the optical absorption, functional group, surface morphology and elementary composition of pure TiO_2 and doped TiO_2 nanoparticles by using UV-Visible spectroscopy, FT-IR, Photoluminescence (PL) -Studies, FE-SEM and EDS analysis [12].

A novel synthesis route of homogeneously manganese-doped TiO_2 nanotubes in a broad concentration range. The scroll-type tri-titanate ($H_2Ti_3O_7$) nanotubes prepared by hydrothermal synthesis were used as precursors. Mn^{2+} ions were introduced by an ion exchange method resulting $Mn_xH_{2-x}Ti_3O_7$. In a subsequent heat treatment, they were transformed into $Mn_yTi_{1-y}O_2$, where y = x/ (3 + x). The state and the local environment of the Mn^{2+} ions in the precursor and final products were studied by the electron spin resonance (ESR) technique. It was found that the Mn^{2+} ions occupy two positions: the first having an almost perfect cubic symmetry while the other is in a strongly distorted octahedral site. The ratio of the two Mn^{2+} sites is independent of the doping level and amounts to 15:85 in $Mn_xH_{2-x}Ti_3O_7$ and to 5:95 in $Mn_yTi_{1-y}O_2$. SQUID magnetometry does not show the long-range magnetic order in the homogeneously Mn^{2+}-doped nanotubes [13].

Manganese doped TiO_2 nanoparticles are synthesized via a simple sol-gel method. The structural characterization of the nanoparticles is done by X-Ray Diffraction and TEM. EDX analysis confirms the incorporation of manganese ions in the Nano crystalline lattice without the presence of any detectable oxide phases. Doping imparts magnetism in TiO_2 and the magnetic response is found to be strikingly different when annealed under two different atmospheric conditions. Vacuum annealed sample shows ferromagnetic behaviour whereas air-annealed sample exhibits complete Para magnetism. Such ferromagnetic behaviour is attributed to the interaction of neighboring Mn^{2+} ions via oxygen vacancies [14].

Thin layers of pure TiO_2 and TiO_2 doped by different amounts of Fe_2O_3 have been prepared by the sol–gel method with tetra isopropyl ortho titanate and $Fe(NO_3)_3$. Physico-chemical properties of catalysts were characterized by BET Adsorption, X-ray Diffraction (XRD), FE-SEM, as well as Raman and UV-Vis spectroscopy. The photo catalytic activity of the obtained materials was investigated in the reaction of complete oxidation of p-xylene in the gas phase under the radiation of UV (_ = 365 nm) and LED (_ = 470 nm) lamps. It has been found that the particle size of all samples was distributed in the range 20–30 nm. The content of the rutile phase in Fe-doped TiO_2 samples varied in the range 6.8 to 41.8% depending on the Fe content. Iron oxide doped into TiO_2 enables the photon absorbing zone of TiO_2 to extend from UV towards visible waves as well as to reduce its band gap energy from 3.2 to 2.67 eV. Photo catalytic activities of the TiO_2 samples modified by Fe^{3+} have been found to be higher than those of pure TiO_2 by about 2.5 times [15].

Titanium oxide precursor solution and manganese oxide precursor solution were prepared by advanced sol gel method. Titanium-manganese oxide mixture solution was prepared by mixing so that a molar ratio 10:1, 50:1, and 100:1 was obtained. The powders dried from the precursor solutions by IR lamp were heat-treated at various temperatures for 1 hour, and measured by X-ray diffractometer. As shown in Fig. 1, the peaks of titanium oxide assignated to anatase structure were confirmed at 500. When the amount of added manganese is increased, the anatase peak shifted to a larger angle. The peaks of manganese oxide were not detected. This result may be caused by the formation of a solid solution of titanium and manganese oxide. Titanium, manganese and titanium-manganese oxide thin films were prepared by spin coating.. When a small amount of manganese was added to the titanium oxide, the UV-Visible absorption spectra were almost the same as that of a titanium oxide only. But, by increasing the amount of manganese, the absorption end shifted to a longer wavelength. This result shows that manganese doped Titanium oxide thin film may be more useful to visible light portions of sunlight and indoor light than a titanium oxide only [16].

TiO2 Nano crystals doped with 1%, 5% and 10% Co/TiO2 and 10% M (M=Fe, Mn and Ni) were prepared by the sol–gel technique and characterized using X-ray diffraction and SQUID. The as-prepared samples are found to be paramagnetic at room temperature, with the magnetic susceptibility following the Curie–Weiss law in the investigated range of 2–370 K. However, transformation from Para magnetism to room-temperature ferromagnetism (RTFM) for the 5% Co/TiO2 was observed by hydrogenating the sample at 573 K while the 1% sample remained paramagnetic. As the percentage of Co was increased from 5% to 10% the Curie temperature increased from 390 K to 470 K determined via extrapolation. Transformation from Para magnetism to room-temperature ferromagnetism (RTFM) was also observed by hydrogenation of 10% Fe/TiO2 at 573 K for 6 h. X-ray diffraction of the hydrogenated sample shows only single phase TiO2 structure suggesting that the observed RTFM may be intrinsic but magnetic studies may suggest the possibility of Fe nanoparticles [17].

Manganese/TiO2 composites are prepared by a solvo-thermal process starting from the precursor's titanium propoxide and manganese nitrate. The solvo-thermal processes are driven at temperatures of 140 °C or 180 °C. The formation of anatase as crystalline TiO2-phase was determined by XRD for preparation conditions at 180 °C. The occurrence of crystalline phases in nanometer scale is determined further by TEM. The prepared manganese/TiO2-composites are further investigated as coating onto viscose textile. The photo catalytic activity of those composites was determined by degradation of organic dye stuff under illumination with UV-light. The effect of photo catalytic dye degradation is also investigated in presence of H2O2. The prepared textile coatings exhibit a high capability for dye decomposition under the chosen arrangement of investigations. For this reason, the prepared coated textile materials could be of high interest for industrial applications, for example, as filter material for cleaning waste water from dyeing processes [18].

Titanium dioxide (Titania; TiO2) is one of the most widely used metal oxide semiconductor in the field of photo catalysis for removal of pollutants. It has been noted that titanium dioxide is a research friendly material as its physico-chemical and catalytic properties can be easily altered as per specific application. Since many years, researchers have tried to modify the properties of titanium dioxide by means of doping with metals and non-metals to improve its performance for photo catalytic degradation (PCD) applications. The doping of various metal ions like Ag, Ni, Co, Au, Cu, V, Ru, Fe, La, Pt, Cr, Ce, etc. in titanium dioxide have been found to be influencing the band gap, surface area, particle size, thermal property, etc. and therefore the photo catalytic activity in PCD. Moreover, photo catalytic activity of doped titanium dioxide has been observed in visible light range (i.e., at wavelength >400 nm). In this review, different synthesis route for doping of metal ions in titanium dioxide have been emphasised. The effect of metal dopant on the structural, textural and photo catalytic properties of titanium dioxide has been reviewed [19].

Various levels of manganese (Mn)-doped ZnO was synthesized by precipitation method. Characterization was carried out by XRD, TEM, SEM, EDX, BET and the band gap measured by UV-visible reflectance. In the XRD pattern of samples, there is no signature of impurity peaks, which could indicate Mn-related secondary phases. The EDX show the amount of Mn doped on ZnO is slightly lower than the theoretical value. The SEM of 1% Mn-doped ZnO illustrated that morphology is well ordered, has low aggregation, and homogeneous distribution of particle size. Results of TEM show that more than 50% of the particles for un-doped and Mn-doped ZnO use between 15 and 35 nm, with 1% Mn doped ZnO having the highest percentage (77%). The BET shows that the surface area of synthesized catalyst increases when the weight ratio of manganese increases up to 1% Mn, but decreases thereafter. The band gap of 1% Mn-doped ZnO is 2.2 eV which is smaller than the un-doped ZnO band gap. The results of characterization show 1% Mn-doped ZnO has the highest surface area, the lowest particles size and the lowest agglomerate. Moreover the calculated band gap of 1% Mn-doped ZnO is lower than others except 0.5%Mn. Additionally, photo degradation of cresols under visible light showed that 1% Mn-doped ZnO had maximum adsorption and rate of photo degradation. In conclusion 1% Mn doped ZnO is suitable as the best photo catalyst to degrade cresols under visible light irradiation [20].

The potential of titanium dioxide (TiO2) semiconductor materials to split water into hydrogen and oxygen in a photo electrochemical cell. The work triggered the development of semiconductor photo catalysis for a wide range of environmental and energy applications. One of the most significant scientific and commercial advances to date has been the development of visible light active (VLA) TiO2 photo catalytic materials. In this review, a background on TiO2 structure, properties and electronic properties in photo catalysis is presented. The development of different strategies to modify TiO2 for the utilization of visible light, including non-metal and/or metal doping, dye sensitization and coupling semiconductors are discussed. Emphasis is given to the origin of visible light absorption and the reactive oxygen species generated, deduced by physicochemical and photo electrochemical methods. Comprehensive studies on the photo catalytic degradation of contaminants of emerging concern, including endocrine disrupting compounds, pharmaceuticals, pesticides, cyanotoxins and volatile organic compounds, with VLA TiO2 are discussed and compared to conventional UV-activated TiO2 nanomaterial. Recent advances in bacterial disinfection using VLA TiO2 are also reviewed. Issues concerning test protocols for real visible light activity and photo catalytic efficiencies with different light sources have been highlighted [21].

III. SIMULATION STUDIES

Materials Studio is an entire displaying and reproduction condition intended to permit Researchers in materials science and science to foresee and comprehend the connections of a material's nuclear and atomic structure with its properties and conduct. Diminish improvement time and expenses with prescient demonstrating and re-enactment programming that gives you a chance to investigate situations, before exorbitant exploratory work. The band structure diagram demonstrates the adjustment in band-crevice for different doping levels, and furthermore the conductivity is additionally examined utilizing this DFT apparatus.

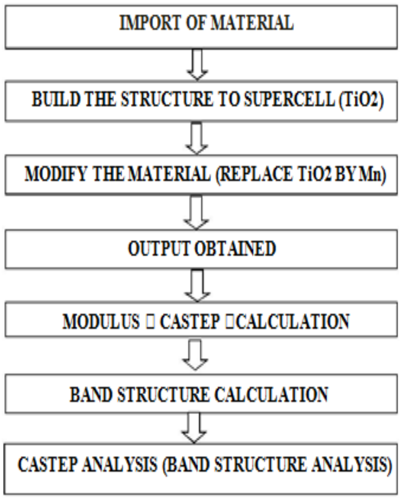


Fig 1: Algorithm

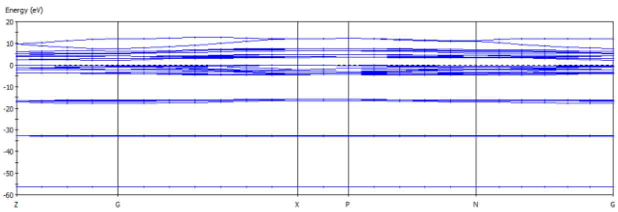


Fig 2: Band Structure of un-doped TiO2

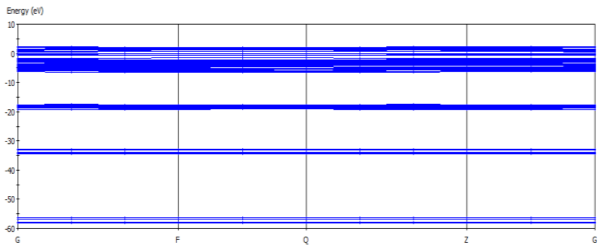


Fig 3: Band structure Mn doped TiO2

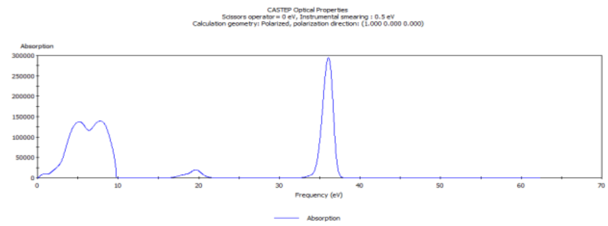


Fig 4: Absorption of un-doped TiO2

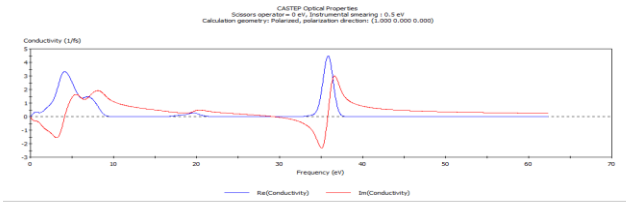


Fig 5: Conductivity of un-doped TiO2

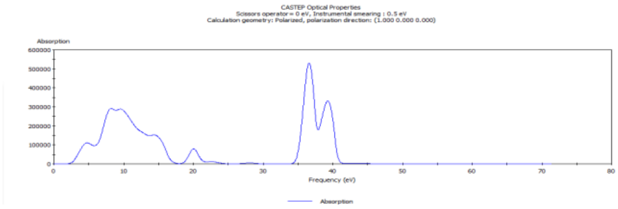


Fig 6: Absorption of Mn doped TiO2

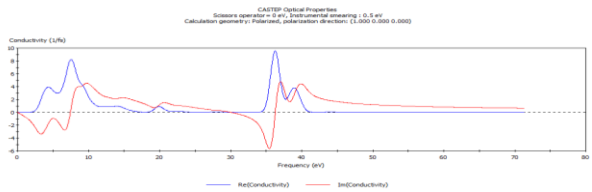


Fig 7: conductivity of Mn doped TiO2

IV. METHODOLOGY: SOL-GEL

Sol-gel is a process in which solid nanoparticles dispersed in a liquid (a sol) agglomerate together to form a continuous three-dimensional network extending throughout the liquid (a gel).

The idea behind sol-gel synthesis is to “dissolve” the compound in a liquid in order to bring it back as a solid in a controlled manner. Basically you mix ingredients that contain molecules that can interconnect together to form bigger molecules and eventually nanoparticles. These nanoparticles, then hook up together to form a gel- network.

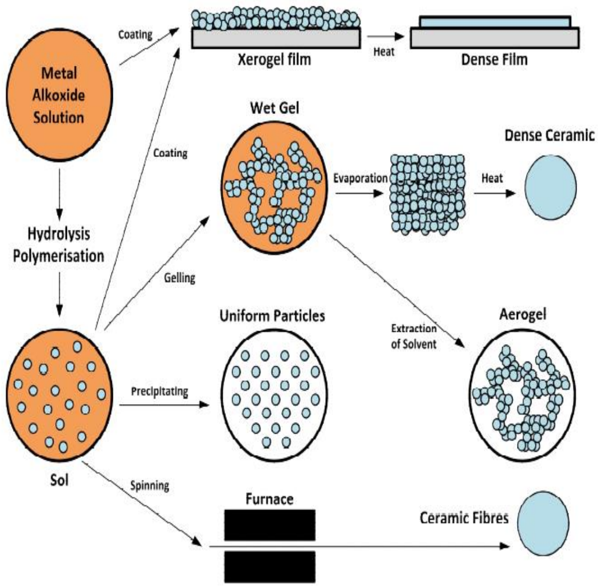


Fig 8: Sol-Gel Process

Advantages of sol-gel method:-

- Cheap and low temperature operation.
- Very thin layers of metal oxide can be obtained.
- Can produce thick coating to provide corrosion protection performance.
- Can easily shape materials into complex geometries in a gel state.
- Can produce high purity products because the composition is highly controllable
- Can have low temperature sintering capability, usually 200-600°C.
- Can provide a simple, economic and effective method to produce high quality coatings.
- Small quantities of dopants, such as organic dyes and rare earth metals, can be introduced into the sol and be finely dispersed in the final product.
- Can be used to make glass with new compositions. High density glass can also be made at low temperatures, without high temperature recrystallization.

V. EXPERIMENTAL DETAILS

Materials Required

Titanyl acetyl acetone, Manganese acetate tetra hydrate, Ethanol, Distilled water are the required materials of analytical grade purchased from sigma Aldrich and few other chemical providers respectively, and were used without further purification.

Preparation

Titanyl acetyl acetone (powder) was mixed in beaker with Ethanol, with continuous stirring using a magnetic stirrer and pipette at 80°C for 1 hr, in required proportions for the synthesis of un-doped Titanium-oxide. The obtained gel was then calcined at 200°C for 12hr in crucibles. Then the formed Xero-gels are heated at 500°C for 12hr in a muffle furnace. Thus the Nanoparticles are formed. (5%, 10%, 15%) Manganese doped Titanium oxide Nanoparticles were synthesized in the similar manner, mixing Manganese acetate tetra hydrate to Titanyl acetyl acetone in ethanol with calculated amount of powder.

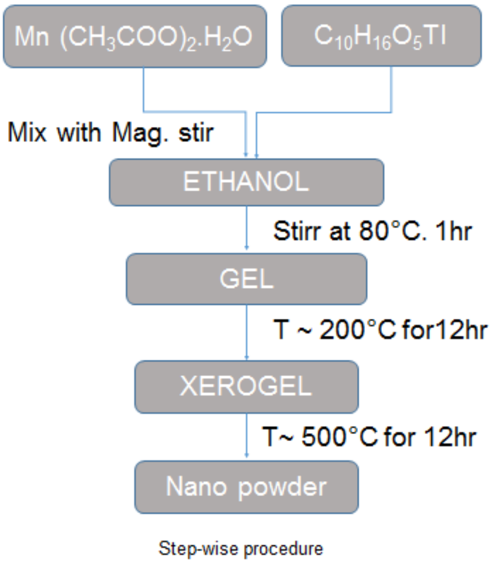
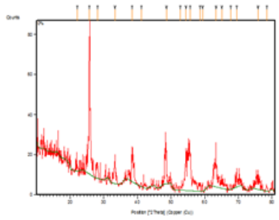


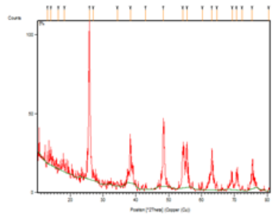
Fig 9: Step-wise procedure

VI. RESULTS AND DISCUSSIONS

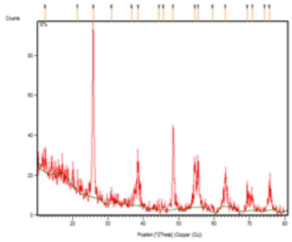
Figure 6 shows a representative XRD pattern for the Mn/TiO2samples (un-doped, 5% , 10%, 15% doped Mn) as prepared. XRD pattern shows the anatase without any impurity peaks indicating Mn is well dispersed within TiO2 lattice.



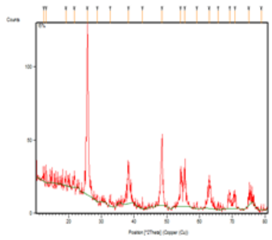
XRD of Un-doped Tio2



XRD of 5% Mn Doped Tio2



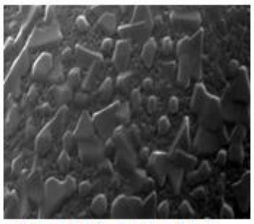
XRD of 10% Mn doped Tio2



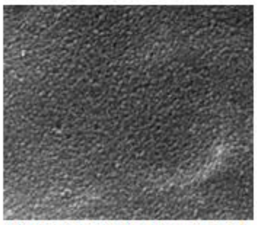
XRD of 15% Mn doped Tio2

Fig 6: XRD results

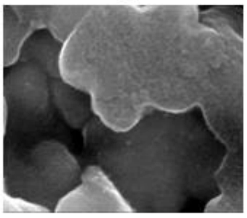
Whereas Figure7 represents SEM analysis with various Mn/TiO2 samples (un-doped, 5% , 10%, 15% doped Mn)showed the size of the particles in less than 50nm. The sample with 15% doped Mn /Tio2 shows the maximum reduction in energy band gap with 40nm.So that, it is activated under visible light.



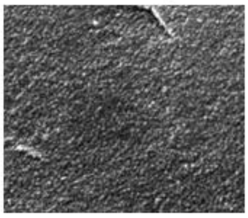
SEM of Un-doped Tio2



SEM of 5% Mn Doped Tio2



SEM of 10% Mn doped Tio2



SEM of 15% Mn doped Tio2

Fig 7: SEM results

VII. APPLICATIONS

The material can be used in the following fields:

- Spin based electronic devices
- Pure inorganic oxide solar cells
- Photo catalyst for degradation organic pollutants
- Feasible water splitting
- Dye-Sensitized solar cells
- Degrading organic contaminants and germs
- Used in paper industry
- Used as a UV resistant material

CONCLUSION

Finally, the required Nanoparticles of un-doped, 5%, 10%, 15% Mn doped TiO2 were prepared by sol-gel technique. 0 This increase in doping proportion of Mn in the oxide material reduced the band gap to a larger extent, so this material is activated under visible light. The simulation studies were carried out using DFT tool and analysis results shows the band-gap was decreased by 0.5eV. Also as the doping level of Manganese increased, the material acquired the property of Ferro-magnetism in room temperature (30°C). Thus the Mn doped TiO2 Nanoparticles were synthesized and its characteristics are studied using XRD and SEM.

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