

Synthesis, characterization and photocatalytic activity of Zn^{2+} , Mn^{2+} and Co^{2+} doped SnO_2 nanoparticles

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ABSTRACT

Nanomaterials with many improved properties have been used in versatile applications. Herein we have synthesized SnO_2 NPs doped with transition metal ions such as Zn^{2+} , Mn^{2+} and Co^{2+} through a facile and inexpensive hydrothermal approach. The synthesized nanomaterials were characterized by XRD, FT-IR, SEM and UV-Vis analysis. The optical properties of the NPs were characterized by using UV-vis and photoluminescence spectroscopy (PLS). Their photocatalytic performances were investigated by degrading methylene blue (MB) dye with UV irradiation. Transition metal doping to SnO_2 NPs improved the photocatalytic activity to degradation of methylene blue dye due to tuning of band gap energy i.e. lowering of band gap energy compared to undoped SnO_2 NPs. The results suggest that the synthesized NPs could be used efficiently for remediation/degradation of environmentally hazardous dyes from waste water or environmental cleanup.

Keywords: Metal doped SnO_2 nanoparticles, methylene blue dye, photoluminescence, UV irradiation.

1. INTRODUCTION

Luxurious lifestyle of humans has brought many unwanted changes in our mother environment which challenges the ecology of earth natural systems resulting in many environmental problems. So it is a very important and urgent challenge to find proper semiconducting material which can produce H_2 and O_2 through a photocatalytic reaction. TiO_2 NPs was discovered in 1972 and is one of the best photocatalysts among the semiconducting metal oxides nanoparticles [1-6]. Rutile structured SnO_2 NPs was studied extensively after TiO_2 NPs because SnO_2 NPs possess high surface area and temperature resistance, low toxicity and high ability does redox reactions with gases [7]. In addition, SnO_2 NPs are n-type semiconducting materials with a band gap of 3.6 eV at 330K with an exciton Bohr radius of 2.7nm [8,9]. Recently Li et al. (2017) used ZnO nanowires doped with Mn^{2+} and Co^{2+} ions to improve its visible-light absorption for photocatalytic degradation of methyl orange (MO) dye [7]. Etacheri et al. (2012) used Mg-doped ZnO NPs for efficient Sunlight drove photocatalysis study [10]. Similarly, Mohamed and Shawky (2018) reported the synthesis of Mn-doped ZnO nanoparticles on CNT support and used for photocatalytic degradation of malachite green dye under visible light [11]. Babu et al. (2017) used Cu^{2+} -doped SnO_2 quantum dots (QDs) for higher photocatalytic activity compared to pure SnO_2 QDs [12]. Zhang et al. (2017) synthesized novel $\text{TiO}_2/\text{Ag}/\text{SnO}_2$ composites photocatalyst for photodegradation of methylene blue (MB) via visible light and found significantly enhanced 9.5 times catalytic activity compared to individual TiO_2 or the binary composite (TiO_2/Ag or $\text{TiO}_2/\text{SnO}_2$) [13]. Zeferino et al. (2019) used indium doped SnO_2 NPs for UV degradation of MB dye and reported that there was no intermediate formation i.e. direct mineralization

during photodegradation compared to the production of intermediate byproducts such as azure A, azure B, and azure C by pure SnO_2 NPs [14].

PrabhakarVattikuti et al. (2018) prepared $\text{SnO}_2\text{-ZnO}$ QDs/ $\text{g-C}_3\text{N}_4$ hybrid for the degradation of pollutants and hydrogen gas (H_2) generation under visible-light irradiation. Also, the synergistic effect of doped oxides increased visible light absorption of the hybrid which enhanced its photoelectrochemical activity as a promising electrode material [15]. Zhang et al. (2011) prepared $\text{SnS}_2/\text{SnO}_2$ nanocomposites with tunable SnO_2 contents and observed superior photocatalytic activity compare to both SnS_2 NPs and physically mixed $\text{SnS}_2/\text{SnO}_2$ composite NPs [16]. Yin et al. (2014) synthesized $\text{SnO}_2/\text{g-C}_3\text{N}_4$ nanocomposite visible light sensitive photocatalysts for methyl orange (MO) degradation under visible light exposure (wavelength ≥ 400 nm) and found much higher efficiency than that of pure $\text{g-C}_3\text{N}_4$ [17]. Gao et al. (2018) developed visible light sensitive photocatalyst $\text{g-C}_3\text{N}_4/\text{SnO}_2\text{:Sb}$ composites by a facile hydrothermal method and tested for degradation of rhodamine B. The test results showed the superior photocatalytic efficiency of $\text{g-C}_3\text{N}_4/\text{SnO}_2\text{:Sb}$ composites compare to $\text{g-C}_3\text{N}_4/\text{SnO}_2$ without doping Sb [18] suggesting promising materials for the potential application in environmental protection. Jiang et al. (2019) prepared yttrium-doped TiO_2 hollow spheres ($\text{Y-TiO}_2\text{HS}$) via a sol-gel method. The as-synthesized materials showed higher thermal stability with Y-doping and enhanced photocatalytic activity of TiO_2 by 3 times compare to un-doped TiO_2HS [19].

Although different methods have been used to synthesize SnO_2 NPs such as sol gel [20], microemulsion [21], hydrothermal [22], co-precipitation [23], chemical precipitation [24] and polyol [25],

all of them use toxic and hazardous chemicals and solvents which are not friendly to humans and environment. Hence it is urgently necessary to find novel and environmentally friendly materials synthesizing by eco-friendly methods for different applications [26-28].

Less toxic semiconductor rutile SnO_2 NPs has high surface area, temperature resistance and sensitivity in reducing environmental

pollutants. Among available photocatalysts, n-type semiconducting SnO_2 (wide direct bandgap of about 3.6eV) is highly efficient in degrading water pollutants [1]. Hence the main objective of the present study was to synthesize novel Zn^{2+} , Mn^{2+} and Co^{2+} ions doped SnO_2 NPs for environmental cleanup, especially degradation of organic toxic methylene blue (MB) dye under UV irradiation.

2. MATERIALS AND METHODS

2.1. Materials.

All analytical grade reagents $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{Co}(\text{OAC})_2$, $\text{Mn}(\text{OAC})_2$ and $\text{Zn}(\text{OAC})_2$ were purchased from Sigma Aldrich (Bangalore) and Milli-Q water was used for the synthesis of nanomaterials by hydrothermal method, degradation of methylene blue dye (Fig. 1) and other studies.

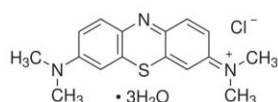


Figure 1. Structure of Methylene Blue (MB) dye.

3. RESULTS

3.1. X-Ray diffraction studies.

Normally X-ray diffraction (XRD) studies are done to find out the crystallinity and phase purity of the synthesized nanomaterials. Sometimes it is used to determine crystallite size of the particles. Initially, a few milligrams of the sample was dispersed in distilled water with sonication and then one or two drops of the dispersion was placed on the copper-grid followed by solvent evaporation for XRD analysis. The XRD patterns of SnO_2 NPs, Zn-doped SnO_2 NPs, Mn-doped SnO_2 NPs and Co-doped SnO_2 NPs are shown in Fig. 2-3. The XRD pattern was identified by comparing with the JCPDdata card No. 96-100-0063. The XRD patterns of Zn-doped (blue), Mn-doped (red) and Co-doped (grey) SnO_2 nanoparticles had the same diffraction peaks as SnO_2 . There were no other sharp peaks to be attributed to zinc, manganese or cobalt elements in the XRD patterns which indicate that doped Zn^{2+} , Mn^{2+} and Co^{2+} ions had no effect on crystalline structure of SnO_2 .

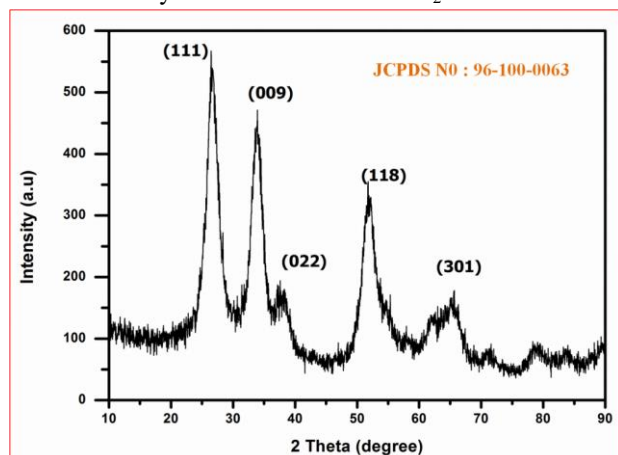


Figure 2. XRD pattern of pure SnO_2 NPs.

2.2. Synthesis of SnO_2 NPs & Zn^{2+} , Mn^{2+} and Co^{2+} doped SnO_2 NPs.

200 mL precursor solution (0.075 M) was prepared by mixing stannous chloride dehydrate and manganese(or cobalt or zinc) acetate dehydrate at the molar ratio of 9:1 in deionized water. Then pH of the solution was adjusted to 10 with ammonia at room temperature by stirring for half an hour. Finally, the as-prepared substrate solutions were kept in a Teflon-lined autoclave and heated at 90°C for 6 h followed by washing with water and drying at room temperature. The same procedure was followed in synthesizing SnO_2 NPs without other precursor solutions.

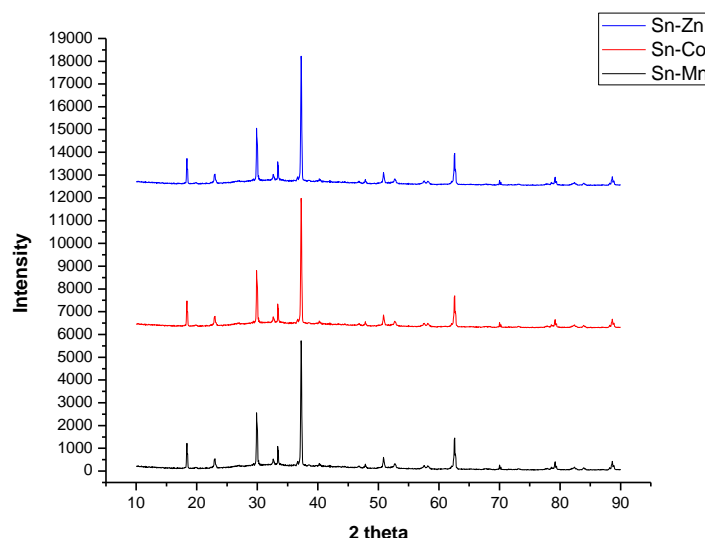


Figure 3. XRD patterns of Zn-doped SnO_2 NPs (blue), Co-doped SnO_2 NPs (red) and Mn-doped SnO_2 NPs (grey).

3.2 FT-IR Studies.

FT-IR analysis is done to detect any functional groups present on the surface of nanomaterials or metal oxide formation.

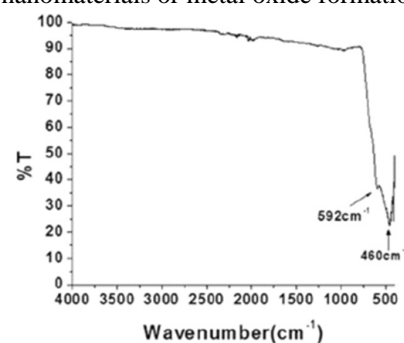


Figure 4. FT-IR spectrum of pure SnO_2 NPs.

The FT-IR spectrum of the synthesized pure SnO_2 NPs is shown in Fig. 4 while that of SnO_2 NPs doped with Zn^{2+} (black), doped with Mn^{2+} (blue) and doped with Co^{2+} (red) shows two representative bands (Fig. 5). The band at around 590 cm^{-1} develops due to Sn-O-Sn anti-symmetric vibration and at 460 cm^{-1} for Sn-O symmetric vibration while band around 3200 cm^{-1} is due to the doping of transition metal. This information confirm the formation of metal oxide bond.

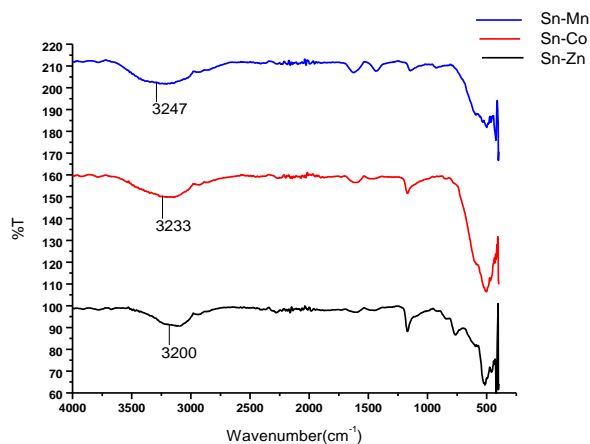


Figure 5. FT-IR spectra of Mn-doped SnO_2 NPs (blue), Co-doped SnO_2 NPs (red) and Zn-doped SnO_2 NPs (black).

3.3. UV-Vis and Photoluminescence studies.

Many parameters influence the optical properties of semiconductor materials. In general, energy gap is the critical one which influences the most in photocatalytic activities. Also, impurity centers and surface roughness tunes its efficiency. In addition, oxygen vacancies can enhance the formation of electron-hole pairs. UV-vis spectrophotometry was used to check its optical properties.

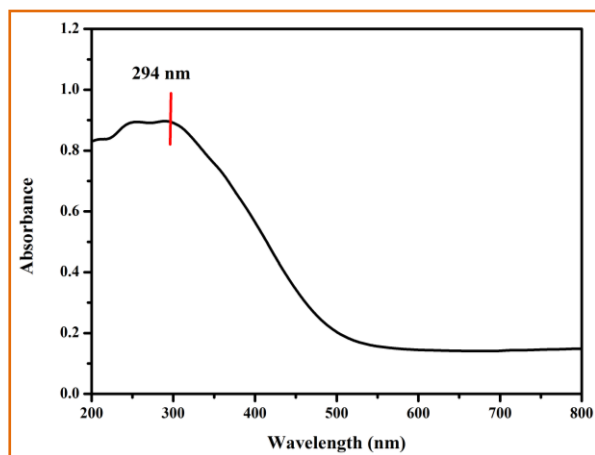


Figure 6. UV-Visible spectrum of pure SnO_2 NPs.

Undoped SnO_2 NPs showed maximum absorbance at 294 nm in UV region (Fig. 6). Figure 7 shows the absorption bands at 249 nm for Mn-doped SnO_2 NPs (blue), 261 nm for Co-doped SnO_2 NPs (red) and 269 nm for Zn-doped SnO_2 NPs (black) respectively. There is a clear blue shift on doping of metal ions on SnO_2 NPs (Fig. 7). Figure 8 shows an emission band at 348 nm in photoluminescence spectrum (PLS) of the synthesized undoped SnO_2 NPs. It suggests that oxygen or other interstitial defects in the crystals may cause this fluorescence response. Figure 9 shows photoluminescence emission band at 249 nm for Mn-doped SnO_2

NPs (blue), 261 nm for Co-doped SnO_2 NPs (red) and 269 nm for Zn-doped SnO_2 NPs (black).

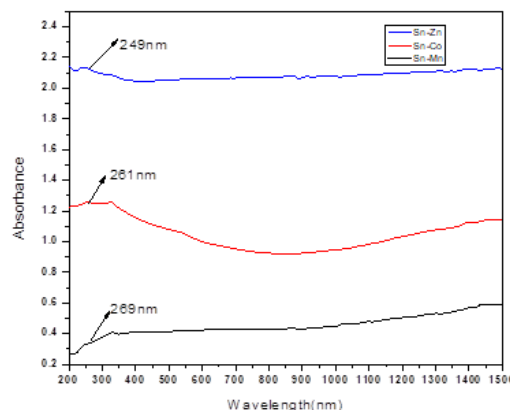


Figure 7. UV-Vis absorption spectra of Zn-doped SnO_2 NPs (blue), Co-doped SnO_2 NPs (red) and Mn-doped SnO_2 NPs (black).

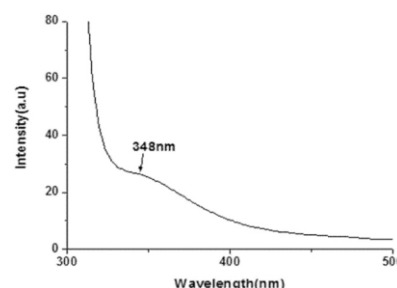


Figure 8. Photoluminescence (PL) spectrum of undoped SnO_2 NPs.

Photoluminescence (PL) is influenced by degree of recombination of the electron-hole pairs which are directly proportional. The PL intensities of doped SnO_2 NPs are lower than that of pure SnO_2 NPs, demonstrating higher fluorescence activity of doped SnO_2 NPs due to trapping of electrons by doped metal ions which suppress the recombination of electron-hole pairs. It is obvious that doped SnO_2 NPs had better optical properties with lower recombination rate.

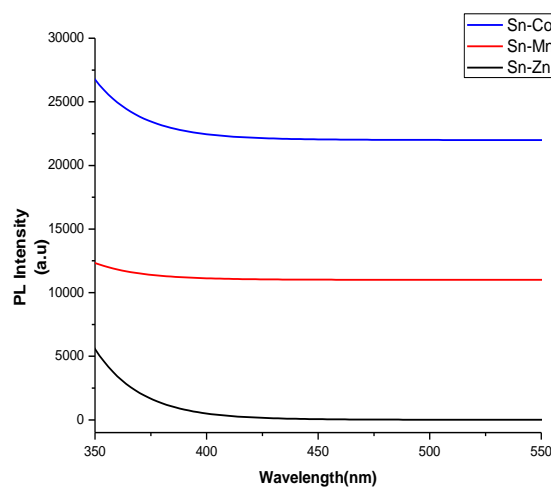


Figure 9. Photoluminescence (PL) spectra of Zn-doped SnO_2 NPs (blue), Co-doped SnO_2 NPs (red) and Mn-doped SnO_2 NPs (black).

3.4. SEM Studies.

SEM analysis was carried out to see the size and shape i.e. morphology and elemental analysis of the synthesized nanomaterials after proper sample preparation. Figure 10 shows

SEM micrographs of Co-doped SnO₂ NPs (Fig. 10a-b), Mn-doped SnO₂ NPs (Fig. 10c-d) and Co-doped SnO₂ NPs (Fig. 10e-f), which documents the shape and morphology of the NPs.

Band gap calculation.

Interstitial defects in SnO₂ NPs crystal system increases the energy gap as well as generates new energy levels lowering energy gap i.e. band gap. In the present study a lower energy gap value from 3.6 to 2.5-1.2 eV is observed (Fig. 11).

The band gap energy (E_g) is estimated using the following equation as $(\alpha h\nu)^2 = A(h\nu - E_g)^n$, where α = Absorption coefficient, A is a constant and $n=2$ for direct and $n=1/2$ for indirect transition. An extrapolation of Tauc plot of ' $h\nu$ ' versus ' $(\alpha h\nu)^2$ ' gives optical energy gap (E_g) value as shown in Fig. 11.

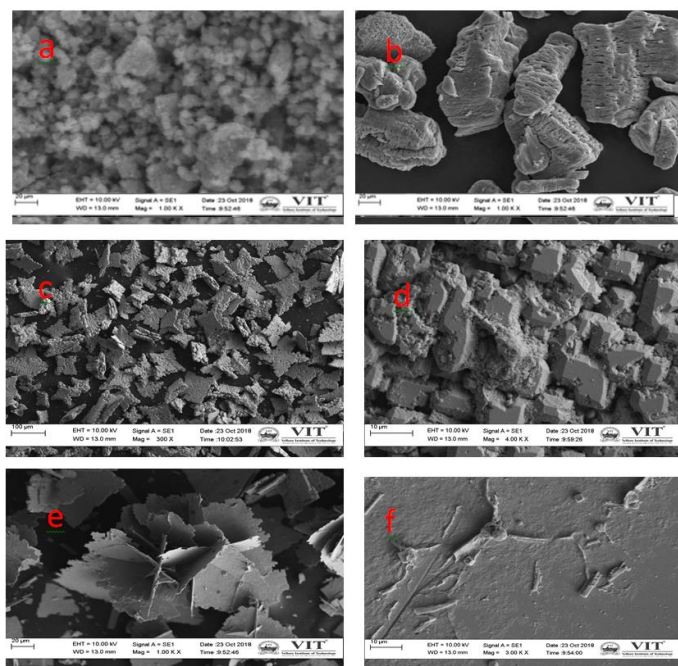


Figure 10. SEM micrographs of pure SnO₂ NPs (a), Mn-doped SnO₂ NPs (b), Co-doped SnO₂ NPs (c, d) and Zn-doped SnO₂ NPs (e, f).

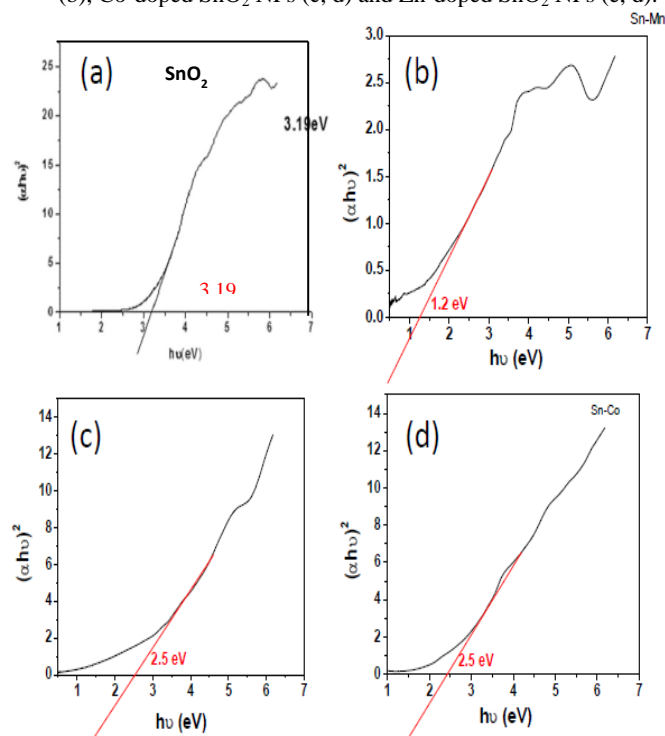


Figure 11. Tauc plots for undoped SnO₂ NPs (a), Mn-doped SnO₂ NPs (b), Zn-doped SnO₂ NPs (c) and Co-doped SnO₂ NPs (d).

The results show that band gap energy of undoped SnO₂ NPs is 3.19 eV, but that of Mn-doped, Zn-doped and Co-doped SnO₂ NPs are 1.2 eV, 2.5 eV and 2.5 eV respectively. It clearly demonstrates that Mn-doped SnO₂ NPs possess lower band gap energy ($E_g=1.2$ eV) than others and it may not be good photocatalyst due to higher possibility of recombination of photogenerated electron-hole pairs. Practically, Zn-doped and Co-doped SnO₂ NPs degraded completely MB dyes within 45 min compared to 75 min for Mn-doped and 120 min for undoped SnO₂ NPs.

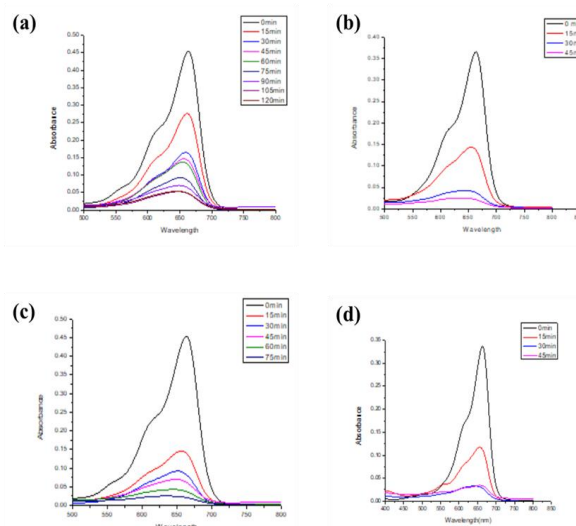


Figure 12. Photodegradation of MB dye (10 mg/L) by undoped SnO₂ NPs (a), Zn-doped SnO₂ NPs (b), Mn-doped SnO₂ NPs (c) and Co-doped SnO₂ NPs (d).

3.5. Photocatalytic Activity Study.

Degradation of MB dye was checked under 125W UV lamp (Hg lamp, λ_{max} 254 nm) by undoped and doped photocatalyst SnO₂ NPs. 60 mL MB dye (20 mg L⁻¹) with 20 mg of catalyst at room temperature. The samples were collected for every 15 min time interval and centrifuged before analysis. Up to 45 min of exposure colour intensity was checked using UV-vis spectrophotometer at 552 nm. One blank experiment without catalyst was done under identical conditions as reference sample (Fig. 12) and no absorbance intensity of MB dye solution was seen at 552 nm after one hour (data not shown) was seen.

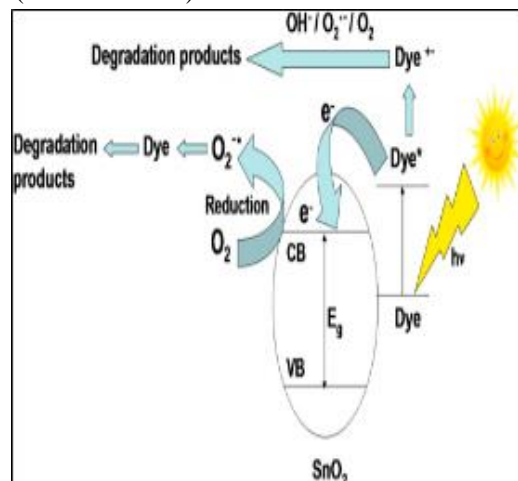


Figure 13. Mechanistic pathways of MB dye photodegradation by using undoped and transition metal-doped SnO₂ NPs.

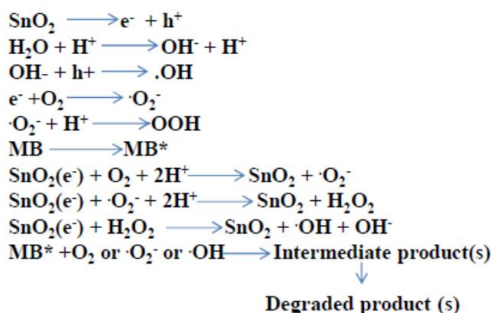


Figure 14. Generation of ROS and Degradation pathways of MB dye in the presence of transition metal doped SnO_2 NPs.

On exposure of UV light (λ_{max} 254 nm) electrons of SnO_2 NPs get excited to the conduction band creating a hole in the valence band. Afterwards electrons in conduction band react with O_2 to form super oxide and the hole in valence band react with H_2O to form OH^\cdot ions i.e. free radicals and super oxide ($\cdot\text{OH}$, $\cdot\text{O}_2^-$). The generated ROS are the oxidizing agents, which oxidizes the dye (Fig. 13). The possible degradation mechanism of dye with catalyst by 254 nm UV irradiation is described schematically in Fig. 12. The stepwise chemical equations followed by degradation of MB by *in situ* generations of ROS such as $\cdot\text{OOH}$, $\cdot\text{OH}$ and $\cdot\text{O}_2^-$ (Fig. 14) [29].

4. CONCLUSIONS

In the present study, we have prepared SnO_2 NPs and SnO_2 NPs doped with Zn, Mn & Co successfully and is characterized by XRD, FT-IR, SEM, UV-Visible and photoluminescence studies. The obtained doped NPs showed the band gap around 2.5 eV which is lesser than the undoped SnO_2 NPs (~ 3.6 eV). We have studied the photocatalytic activity of both undoped and doped SnO_2 NPs with respect to time. Further we have studied the effect

Also, the rate of photodegradation of MB dye was checked with varying doses of catalyst (5, 10, 20 mg) and the degradation kinetics increased with the increasing dose of catalyst (Fig. 15a) i.e. the time of degradation decreased from 70 min to 40 min.

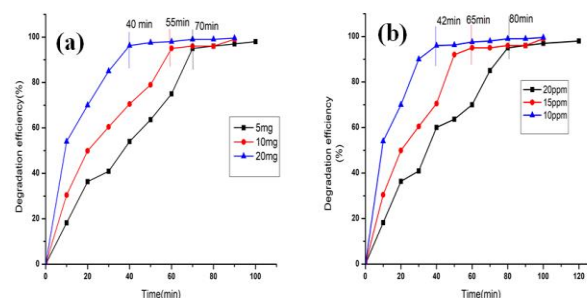


Figure 15. Photodegradation of MB dye: (a) effect of catalyst dosage (5–20 mg) on MB dye (10 mg/L) and (b) effect of dye concentrations (10–20 mg/L) at a catalyst dose of 10 mg.

Similarly, the rate photodegradation was checked with varying concentrations of MB dye (10, 15, 20 mg/L) at a constant catalyst dose of 20 mg and the rate of degradation decreased with increasing dye doses from 10 mg/L to 20 mg/L i.e. the time of degradation increased from 42 min to 80 min (Fig. 15b).

of catalytic doses and the effect of dye concentration on the photodegradation of MB dye. These doped SnO_2 NPs could be a promising photocatalyst in degrading textile dyes compared to undoped SnO_2 NPs in the coming days and would solve demanding environmental pollution caused by industrial activities, namely textile industries throughout India and abroad.

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