INTERNATIONAL JOURNAL OF INNOVATIVE RESEARCH & DEVELOPMENT

Visible Light Photocatalytic Activity Of Manganese Doped Tio_2 Nanoparticles

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Abstract:
In this paper we report the successful synthesis of manganese ($Mn^{2+)}$ doped TiO_2 nanoparticles by sol-gel method. Optical properties of the nanoparticles were characterised by UV-Vis spectrometer in the range 200-900nm and a photoluminescence spectrometer to study the emission spectra of both doped and undoped particles. The UV-Vis spectra of the doped samples shows signature of peaks in the visible region, attributed to the charge transfer transitions between the metal ion d electrons and the conduction or valence band of TiO_2. XRD study shows that upon doping with Mn^{2+} the crystallite size decreases inferring that the dopants effectively inhibits TiO_2 grain growth by staying at grain boundaries . Photocatalytic activities of the TiO_2 samples modified by Mn^{2+} ions have been found to be higher than that of pure TiO_2.

Keywords: *Sol-gel method, Mn^{2+} doped TiO_2 nanopowders, photocatalytic activity.*

Introduction

TiO_2 is a novel inorganic material with a wide range of applications in the field of photocatalysis, photovoltaics, sensors, batteries, potential tool in cancer treatment, self cleaning coatings[1-3] etc. Despite of being versatile TiO_2 has however a major drawback, its wide band gap (3.2eV) restricts all photon driven applications to be activated under visible range . In order to remove such anomalies and extend its absorption in the visible region dye sensitisation, external surface modification and band gap tailoring has been widely focused.Dye sensitisation and external surface modification however requires use of a second semiconductor with a smaller band-gap or other sensitizer to compensate deficit of charge carriers. So band gap tailoring by doping is frequently studied. Doping with various metal ions has been attempted to improve the photocatalytic activity and optical absorption of TiO_2[4]. In our paper we have studied how manganese doping enhances the photocatalytic activity of TiO_2 nanoparticles by using bromophenol blue as a probe

Materials and Method

Preparation Method

The preparation of nickel doped TiO_2 nanomaterials was carried out with two different manganese. concentrations 3%, 5% using sol-gel method employing titanium isopropoxide, isopropanol manganese acetate dihydrate $Mn(CH_3COO)_2.2H_2O$ with the aforementioned concentration.

Characterisation Details

The phase structure and particle size of the materials are determined using Rigaku Miniflex CD 10041 XRD unit with copper target and λ=1.54 angstrom.The elemental composition are known from energy dispersive X-ray analysis(EDX) equipped with a JEOL JSM 6390 LV scanning electron microscope (SEM). High resolution transmission electron microscope, images are observed with JEM-2100 200kV JEOL. Diffuse Reflectance Spectra (DRS) are are taken with Shimadzu-2450 UV-Vis spectrometer.The photoluminescence (PL) measurements at room temperature are recorded with PERKIN ELMER LS 55 fluorescence spectroscopy.

Results And Discussions

XRD Analysis

The XRD patterns of the doped and undoped nanoparticles shown in Fig 1 represents tetragonal anatase phase (JCPDS card no 21-1272. With the increase in the added amount of

manganese ions in the host lattice the peak slightly shifts(inset Fig 1) towards the low angle side indicating well incorporation of manganese ion in the doped sample.

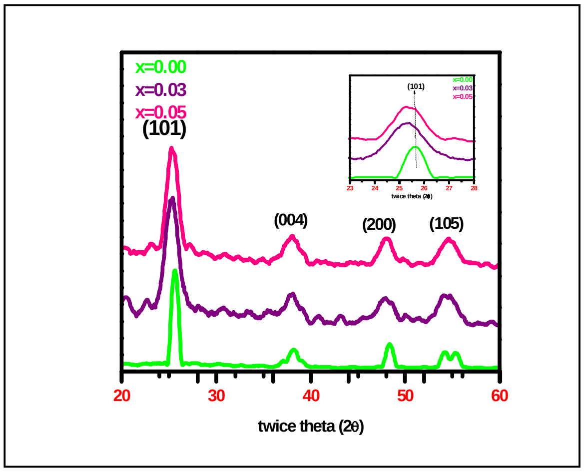
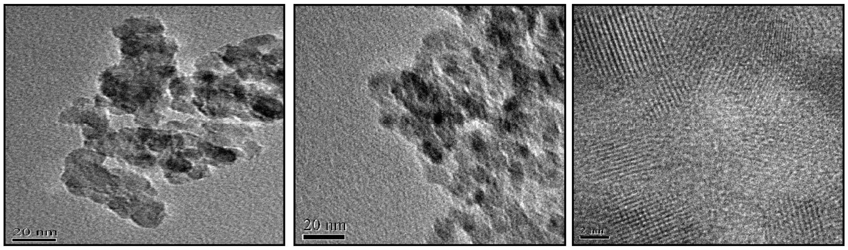


Figure 1: XRD of undoped and Mn^{2+}(x=0.03,0.05)

The mean size of the crystallites in the sample estimated by FWHM of the XRD peak $2\theta=25.4^0$ have been found to be 15nm and 6nm using the Debye-Scherrer equation[5].

TEM

Fig 3(a),(b) shows the TEM images of undoped and manganese doped TiO_2 nanoparticles. Fig 3(c) shows the high resolution image.



(a) (b) (c)

Figure 3: (a) TEM image of TiO_2 nanoparticles (b)TEM image of Mn^{2+} doped TiO_2 nanoparticles (c) HRTEM image of doped TiO_2 nanopartilces.

The particle size for pure and doped samples are calculated to be 17nm and 8nm respectively.. The doped samples show presence of some amorphous phase.

EDX

The presence of manganese in the doped sample is confirmed with EDX.

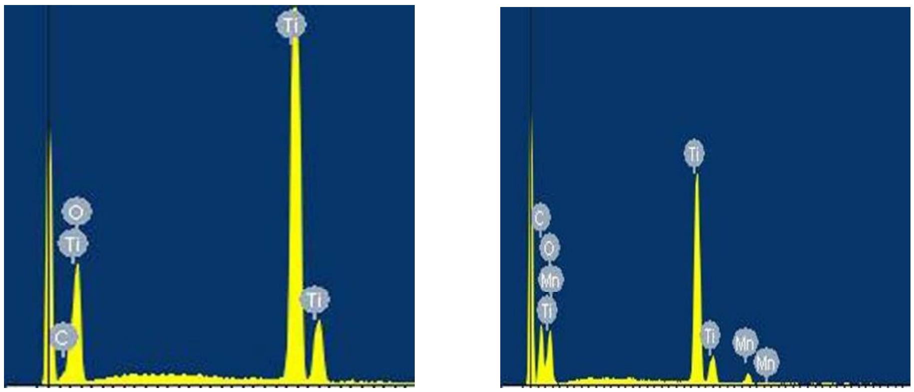


Figure 4(a),(b): EDX spectra of undoped and manganese doped TiO_2

Fig 4(a) and 4(b) shows the EDX spectra of undoped and manganese doped TiO_2 nanoparticles.

Uv-Vis Spectra

The UV-Vis spectra of the doped and undoped TiO_2 is shown in Fig (5).Mn^{2+} doped TiO_2 exhibits a peak in the visible region (592 nm) coming from $^6A_{1g}$ $^4T_{1g}$ [6].

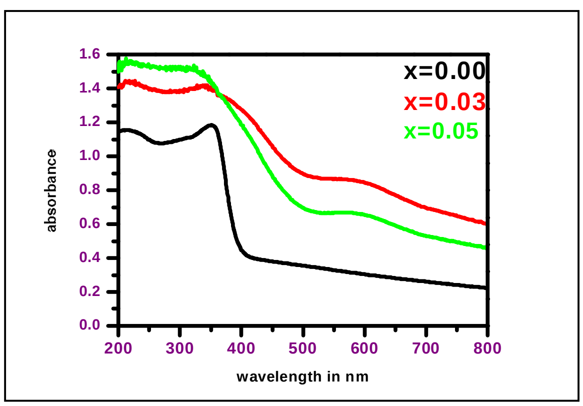


Figure 5: Uv-Vis spectra of undoped and Mn^{2+} doped TiO_2

The band gap of the sample calculated by using Kubelka-Munkplot[5] is found to be 3.2eV(x=0.00),1.95eV(x=0.03), 2.3 eV(x=0.05) . The decrease is due to the introduction of some new energy levels in the band gap of the host lattice.

Photoluminescence spectra

The PL spectra shown in Fig 6 is obtained on exciting the material at 340 nm. The UV emission is arising due to phonon assisted indirect transition [7],438 nm is due to self trapped exciton localised on TiO_6 octahedra [8].The peaks at 463 nm and 537nm is due to the oxygen vacancies[9] . The peak at 487 nm is due to charge transfer transition from Ti^{3+} to oxygen anion in TiO_6^{2-}[10].

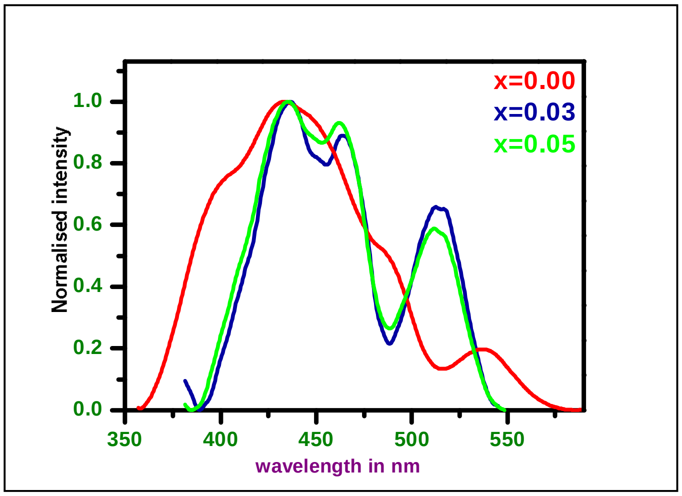


Figure 6: PL spectra of x=0.00, x=0.03,x=0.05

The doped samples are red shifted due to the band tailing effect produced by various defects[5].

Photocatalytic Activity

The photocatalytic degradation of bromophenol blue by manganese doped TiO_2 nanoparticles (x=0.03) have been studied by irradiating the samples under visible light.. Fig 7(a),(b) shows the absorbance curve of undoped and manganese doped TiO_2 nanoparticles. Fig 7(c) shows the degradation efficiency of the doped and undoped samples subjected to different irradiation times. The percentage degradation of the dye loaded with undoped catalyst is found to be only 21.6 % and remains constant with respect to different irradiation times.

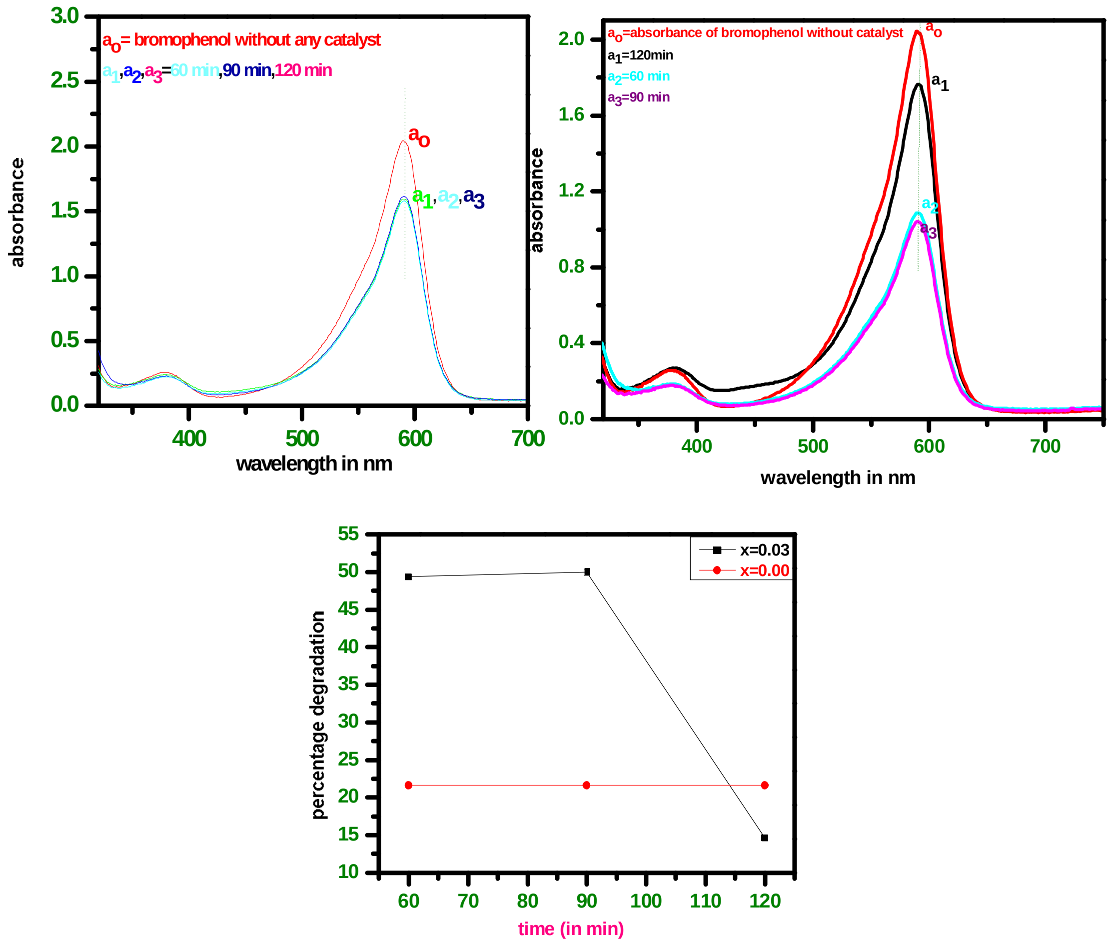


Figure7:(a)absorbanceforx=0.00(b)absorbance for x=0.03 (c) degradation efficiency for undoped and doped samples loaded into the dye and subjected to different irradiation times: t=60 min, t=90 min, t=120 min.

The increase in the efficiency is due to creation of some trap states due to manganese doping that inhibits the electron –hole recombination rate from inside of the material to the surface[11].

Conclusion

TiO_2 and manganese doped TiO_2 are prepared by sol-gel method.XRD patterns reveal the anatase phase in the prepared sample. The mean grain size of the doped sample is found to be less than 10 nm inferring that doping hinders the growth of the samples.The photocatalytic activity of the synthesised sample carried under visible irradiation indicates that manganese doped TiO2 nanoparticles show better photocatalyti activity than the undoped ones.

Acknowledgements

We are thankful to Sophisticated Analytical Instrument Facility (SAIF), NEHU, Shillong for helping us in providing the HRTEM images. We are also thankful to the DST for financial support to the project SR/NM/NS-98/2010(G)/TUPHY1.

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