International Research Journal of Engineering and Technology (IRJET) e-ISSN: 2395-0056
Volume: 04 Special Issue: 09 | Sep -2017 www.irjet.net p-ISSN: 2395-0072

One Day International Seminar on Materials Science & Technology (ISMST 2017)
4th August 2017
Organized by
Department of Physics, Mother Teresa Women's University, Kodaikanal, Tamilnadu, India

Mechanistic investigation of FeO/MnO/ZnO nanocomposites for UV light driven photocatalytic performance

Shanmugam Vignesh[1], M. Sivakami[2], P. Muniyappan[3], Jeyaperumal Kalyana Sundar[4]

[1,2,3,4] *Materials science Laboratory, Department of Physics, Periyar University, Salem – 636 011, Tamil Nadu, India*
**jksundar50@gmail.com, vigneshattur1@gmail.com*

Abstract: *The FeO/MnO/ZnO nanocomposites (FMZ NCs)) which were prepared by ultrasonication assisted precipitation method and investigation of their mechanical and photocatalytic activity were analysed. 10M at % of Fe and Mn metal ions have mixed together ZnO nanomaterial to enhance the optical, luminescence and photocatalytic properties studied via XRD, SEM, EDX, UV-Vis DR Spectroscopy, PL Spectroscopy and photocatalytic performance with their results are discussed. Optical bandgap should be blue shift from 3.18 to 3.04eV, and broad photoluminescence (PL) peak appears around 490nm were corresponds to blue emission region. The photocatalytic activity of the as-prepared FMZ NCs for degradation of MB dye under the UV light irradiation were examined and the FMZ NCs will be time taken of 300 mins in reaches of degradation has 90%. The FMZ of Photocatalytic reaction kinetics will be high compare than PZ.*

Keywords: Photocatalyst, Blue emission, Nanocomposites, UV-light, Degradation

1. Introduction

Nanostructured semiconducting metal oxides are being widely utilized in the fields of sensors, catalysis optical nano devices, electronics, and photoactive properties. Being a wide band gap and multi-disciplinary among the semiconductor, Zinc oxide (ZnO) is one of the most widely investigated semiconductor photocatalyst owing to its availability, non-toxic nature, stability, good resistance to photo corrosion and biological stability. However, to efficiently use ZnO in practice as an air and water decontamination agent, wide bandgap material (~3.37 eV), large excitonic binding energy (60 meV) and can only be activated by UV light with a wavelength equal or lower than 385 nm to trigger the e^-/h^+ separation and its due to easy recombination together [1, 2]. In addition of effective metal ions (tin oxide (SnO), iron oxide (FeO), manganese oxide (MnO), copper oxide (CuO) etc.,) doping in ZnO will be moral results in improved optical, and catalytic properties also increases prospects for their utilization.

2. Synthesis

In Precursors of Zinc nitrate (0.1M), iron II nitrate (0.01M) and manganese acetate (0.01M) and 0.1g of polyvinyl pyrrolidone (PVP) were dissolved in 200 ml of DI water and 50ml ethanol through continuous stirring for 10 hours. Simultaneously, 0.3M of NaOH is added (pH=9) to the particular solution for which resulting in a dark precipitate [3]. This solution was heated by microwave oven at 450W for 20mins with their ultrasonicated in 30 mins for getting a dispersing nano materials. The obtained product was placed in a hot air oven at 120°C for 8 hours, finally it is moved to anneal in the furnace at 600°C for 2.5hr to stabilize [2] the FMZ nanocomposites. A similar procedure was followed to synthesis of with Fe, and other Mn also undoped ZnO, and it's labelled as follows; (Fe: Mn-0M%: ZnO (PZ), Fe-0.01M%: ZnO (FZ), Mn-0.01M%: ZnO (MZ) and Fe-0.01M%: Mn-0.01M%: ZnO (FMZ)).

One Day International Seminar on Materials Science & Technology (ISMST 2017)
4th August 2017
Organized by
Department of Physics, Mother Teresa Women's University, Kodaikanal, Tamilnadu, India

3. Results and Discussion

3.1 Structural analysis

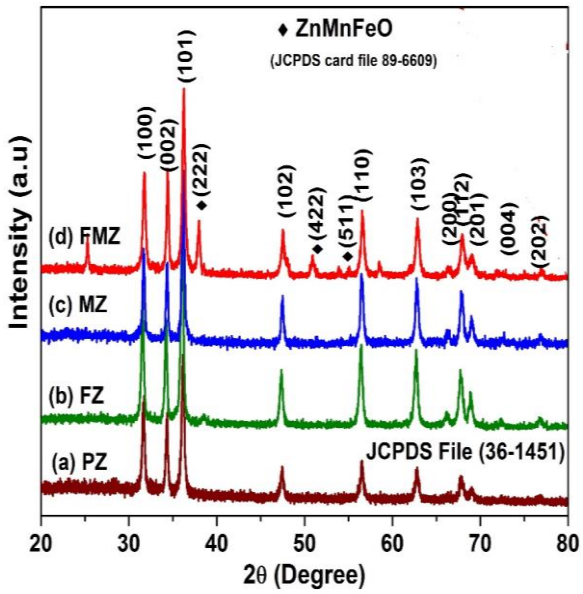

Fig. 1 XRD pattern of prepared samples

The phase characters of prepared samples are studied using powder X-ray diffractometer (Rigaku miniflex II). XRD spectra show broad peaks at the positions of (100) and (101) which are in good agreement with the standard ZnO (JCPDS Card file 36-1451, a = b = 3.249 Å, c = 5.206 Å) and indexed to the hexagonal wurtzite structure of ZnO having space group P63mc [3]. Furthermore, it can be seen in doping materials (FZ, MZ and FMZ) there is obviously change in the ZnO peaks with the existence of Fe and Mn peak, which indicates ZnFeMnO have being the Zn oxides lattices and it will be confirmed to JCPDS card file. XRD pattern show good crystallinity, and there is no other impurity peaks are observed, and it's confirmed they have single-phase sample formation. The crystallite size was estimated using Scherrer's formula, ($D = (k\lambda)/\beta\cos\theta$) for the most prominent X-ray diffraction peak corresponding to (101) peak. Where, β = full width half maximum (FWHM), K = grain shape dependent constant (0.9), λ = wavelength of incident beam (1.5406 Å), θ = Bragg Reflection angle in degree. The deduced crystallite sizes are ranging from 57-32nm for different NPs (Table.1).

Table.1 Structural parameters of undoped and FMZ ZnO nanocomposites

S. No	Samples	Crystalline size (nm)	Lattice Parameters	
			a=b (nm)	c (nm)
1.	PZ	57	3.2708	5.2084
2.	FZ	48	3.2697	5.2168
3.	MZ	39	3.2674	5.2278
4.	FMZ	32	3.2531	5.2307

3.2 Surface Morphology analysis:

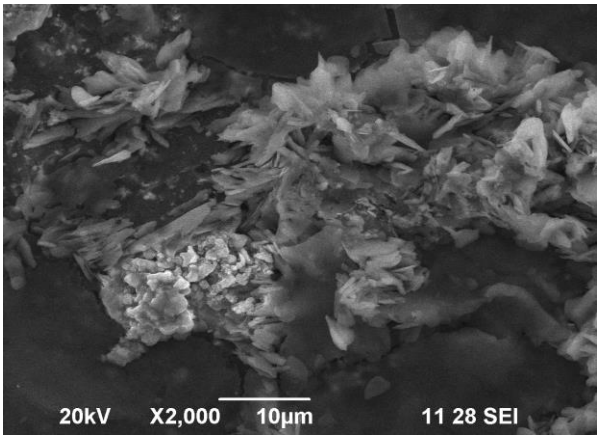

Fig.2 SEM images of FeO/MnO/ZnO nanocomposites

Scanning Electron Microscopy (SEM) is one of the capable techniques for the surface analysis of the samples and to investigate the size also. Using SEM - JEOL Model JSM 6390LV, the surface morphology of FMZ nanocomposites were recorded and shown in Fig.2. It is observed that the synthesized nanoparticles are almost in spherical and flower like morphology shape and it has uniformly distributed throughout the surface. Compositional analysis using EDAX was performed for FMZ samples (Fig.3) and is in very good agreement indicating nominal doping level and atomic percentage of Zn, O, Fe, Mn and C. FMZ composites is in pure phase with an approximate stoichiometry atomic ratio of the elements (Zn: 20.49, Fe:8.98, Mn:9.71, O:29.42 and C:39.40).

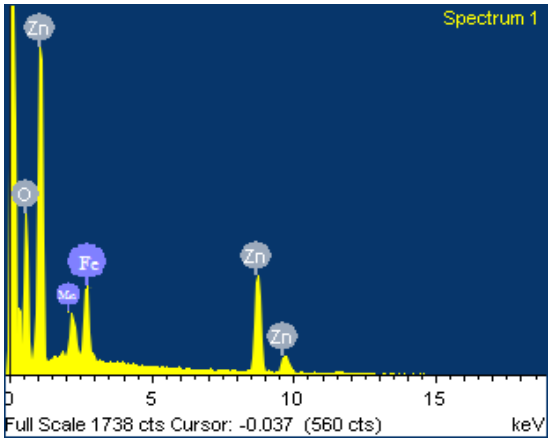

Fig.3 EDAX Spectrum of FMZ NCs

3.3 UV- Vis Diffuse Reflectance Spectroscopy

The absorption spectra (Fig.4) of all prepared samples are analyzed using UV- Vis Spectroscopy (Ocean Optics USB4000 Spectrophotometer). The cut-off wavelength for PZ is 243 nm, whereas all other doping nanoparticles have much more defect of red shift upto 250, 252 and 261nm also [5]. The doping metal ions with their electron density in ZnO leads to change in the conduction band level of the nanoparticles and give modification to the particular bandgap when compared to PZ. These shifts towards the higher energy wavelength of UV- light suggesting the bandgap narrowing in the doped compounds which is confirmed via tauc plot analysis of spectroscopic data (Fig. 5). The tauc plots are drawn using Tauc equation $(\alpha h\nu)^2 = A\,(h\nu - Eg)$, where, ν is the frequency of light, A is a constant, h is the planck's constant, and Eg is energy bandgap of the material.

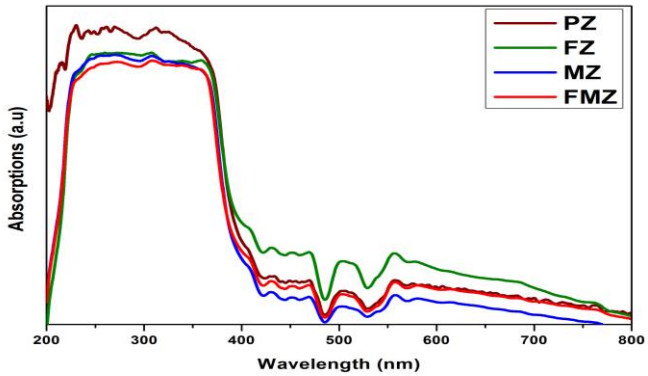

Fig.4 Optical absorption spectra

3.4 Bandgap Analysis:

The bandgap calculated for the PZ, FZ, MZ and FMZ nanocomposites were 3.18, 3.16, 3.1 and 3.04eV respectively and it is observed that the bandgap decreases with adding in the dopant ions (at 10%) with the variation from 3.18eV to 3.04 eV. The percentage of dopant material is playing a vital role in the determination of the bandgap and this tuning the bandgap can be applied to field of opto electronics and photocatalyst properties.

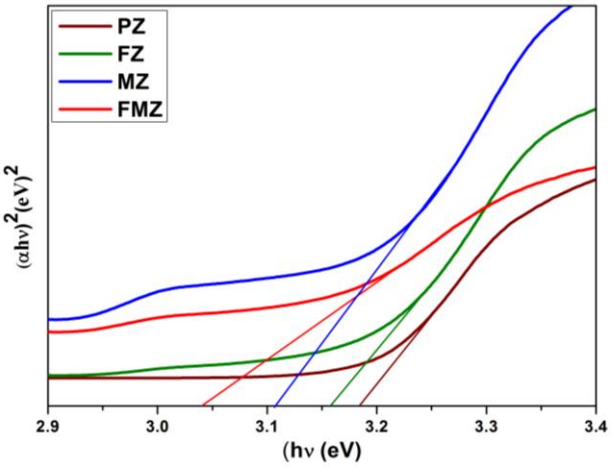

Fig.5 Bandgap calculation via taut plot

3.5 Photoluminescence Spectroscopy

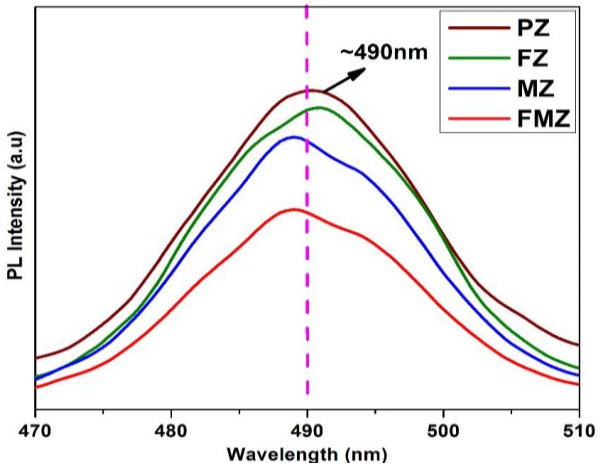

Fig.6 PL Spectra of synthesized samples

The visible photoluminescence (PL) spectroscopy is an effective technique to study the electronic band structure and charge carrier trapping, immigration and transfer which is carried out by Perkin Elmer LS45 spectrometer. All the samples have sharp emission (Fig.6) band around 490nm in the blue region due to the emission from band to band transition (Excitation wavelength λ = 320nm) and they are related to non-stoichiometric intrinsic defects and the same may be caused by the occurrence due to nature of oxygen vacancy [6]. Likewise, FZ, FZ and FMZ nanocomposites exhibiting the low intensities, by means good probability of electron-hole recombination, which allows it for numerous applications like photocatalyst and LEDs.

3.6 Photocatalytic activity

The time dependent photocatalytic activity of the as-prepared PZ, FZ, MZ and FMZ photocatalyst by means 0.1g of catalyst was added into a 100-mL of Millipore water with 20ppm of MB solution and kept ready for the degradation process. A high-pressure halogen lamp with the biggest emission wave of 370 nm was used as the UV light source.

3.6.1 The degradation process of MB

To understand the photocatalyst degradation of prepared NCs and am chosen the MB in the presence of nanocomposites under UV light irradiation. UV–Vis spectra changes in the dye solution over various time intervals (Fig. 7). Hence, the main absorption peak of MB molecules locating at 664 nm in the presence of esteemed FMZ nanocomposites decreases rapidly with extension of the exposure time [7]. For undoped, FZ and MZ nanocomposites have 59 % MB was degraded in the time of 300 mins, and the FMZ NCs has in extreme in colorless the same dye at 91% at the same time. Decomposition efficiency (Fig. 8) can be calculated by using the formula,

$$(D\%)=(C_0-Ct)/(C_0)*100$$

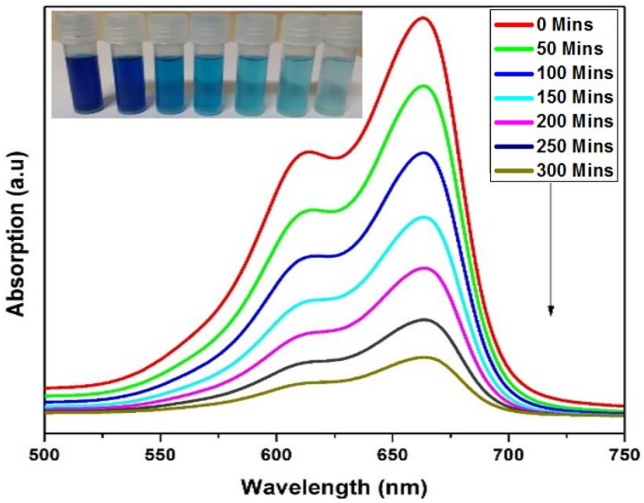

Fig. 7. UV-Absorption Spectra of MB dye degradation

In observed photocatalytic efficiency of FMZ nanocomposites was comparatively higher than others. Reaction kinetics of FMZ nanocomposites being 2.8 times higher than PZ nanocomposites [8]. Reaction mechanism as follows (eqn 1 to 4)

$ZnO + h\nu \rightarrow ZnO + (e^- + h^+)$ -------- (1)
$e^- + O_2 \rightarrow O^-_2$ -------- (2)
$h^+ + OH \rightarrow OH\cdot$ -------- (3)
$OH/O^-_2 + dyes \rightarrow O_2 + H_2O$ -------- (4)

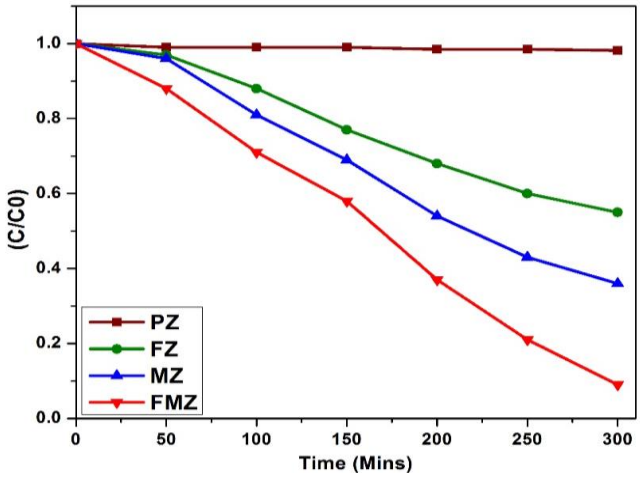

Fig. 8. Photocatalytic degradation efficiency of MB dye under UV light in 300 Mins

4. Conclusion

Novel self-assembled NCs were synthesized by a facile, low-cost, microwave assisted precipitation approach and their structural, optical, and photocatalytic performances were investigated. The XRD pattern reveal the formation of prepared samples are hexagonal wurtzite structure with average crystalline size of ~57nm. SEM images reveal the FMZ NCs which are in spherical and flower like shape. The UV-DRS spectra reveal that significant decreases in optical bandgap of single and co-doping of Fe and Mn ions (3.18eV to 3.04 eV). Interestingly, all the samples have good luminescence property with the strong blue emission at 490nm, and hence they are very useful in the fabrication of blue LED devices and increases the charge separations of electron-hole recombination. The investigation of photocatalytic activity indicated that the FMZ NCs has influenced in maximum degradation efficiency (91%) in degradation of MB under UV irradiations for 300mins. Hence in the catalyst showed significant capacities of optical and environmental purification.

References

[1] V. Pandiyarasan S. Suhasini J. Archana M. Navaneethan M. Abhijit Y. Hayakawa H. Ikeda et al, Applied Surface Science, 2016, 12, 202

[2] Ravichandran, N. Chidhambaram, A. Thirumurugan, S. Velmathi and S. Gobalakrishnan, RSC Adv., 2016

[3] Bin Yang, Wenwu Cao, and Michael N. R. Ashfold ACS Appl. Mater. Interfaces 2016, 8, 16379−16385

[4] Devulapalli Amaranatha Reddy, Deok Hyeon Kim, Seuk Joo Rhee, Bo Wha Lee and Chunli Liu Reddy. Nanoscale Research Letters 2014, 9, 20

[5] Prashant K. Sharma, Ranu K. Dutta, R. J. Choudhary and Avinash C. Pandey CrystEngComm, 2013, 15, 4438

[6] Y.J. Zhai, J.H. Li, X. Fang, X.Y. Chen, F. Fang, X.Y. Chu, Materials Science in Semiconductor Processing 26 (2014) 225–230

[7] Fernanda C. Romeiro, Juliane Z. Marinho, Anielle Christine A. Silva, Nilo F. Cano, Noelio O. Dantas, and Renata C. Lima J. Phys. Chem. C 2013, 117, 26222−26227.

[8] Mohammed M. Rahman, Hasan B. Balkhoyora and Abdullah M. Asiri RSC Adv., 2016, 6, 29342

Acknowledgement: The authors thanks to the UGC for the financial support through the BSR research scheme.

Biographies

Jeyaperumal Kalyana Sundar is an Assistant Professor at Department of Physics, Periyar University, Salem, Tamilnadu, India. He received Ph.D. (Physics) from Madurai Kamaraj University, Madurai. He has an eight years post graduate teaching experience.

Shanmugam Vignesh is a Research Scholar at Department of Physics Periyar University, Salem, Tamilnadu, India. He is doing research in nano photocatalytic, electrochemical, sensor devices and their studies.