Hindawi Publishing Corporation
Journal of Nanomaterials
Volume 2014, Article ID 371720, 6 pages
http://dx.doi.org/10.1155/2014/371720

Research Article

Tunable Band Gap Energy of Mn-Doped ZnO Nanoparticles Using the Coprecipitation Technique

Tong Ling Tan, Chin Wei Lai, and Sharifah Bee Abd Hamid

Nanotechnology & Catalysis Research Centre (NANOCAT), Deputy Vice Chancellor (Research & Innovation), Institute of Graduate Studies, University of Malaya, 50603 Kuala Lumpur, Malaysia

Correspondence should be addressed to Sharifah Bee Abd Hamid; sharifahbee@um.edu.my

Received 14 October 2013; Accepted 17 December 2013; Published 28 January 2014

Academic Editor: Clare C. Byeon

A simple coprecipitation technique was introduced to form manganese (Mn) doped on zinc oxide (ZnO) nanoparticles effectively. Based on our morphological studies, it was revealed that mean particle size was increased while bigger agglomeration of nanoparticles could be observed as the amount of concentration of Mn was increased. Interestingly, it was found that the position of the absorption spectra was shifted towards the lower wavelength (UV region) as correlated with the increasing of Mn dopants concentration into ZnO nanoparticles. This result inferred that optimum content of Mn doped into the ZnO nanoparticles was crucial in controlling the visible/UV-responsive of samples. In the present study, 3 mol% of Mn dopants into the ZnO nanoparticles exhibited the better UV as well as visible light-responsive as compared to the other samples. The main reason might be attributed to the modification of electronic structure of ZnO nanoparticles via lattice doping of Mn ions into the lattice, whereas excessive Mn dopants doped on ZnO nanoparticles caused the strong UV-responsive due to the more 3d orbitals in the valence band.

1. Introduction

Nowadays, most countries are facing environmental pollution problems and thus the awareness of people upon this matter was increased tremendously. Water is an essential source for human beings and it was shown that the demand of clean and safe drinking water is rising; therefore, the use of the nano semiconductor material on photocatalytic oxidation for oxidizing the toxic pollutant has become of great interest in recent material research field [1].

Zinc oxide (ZnO) is an essential semiconductor with direct band gap of 3.3 eV and high excitant binding energy of 60 meV. Due to its potential application in many areas such as optoelectronic devices, solar cells, chemical sensor, and photocatalyst hence, it has attracted the attention of more and more researchers and scientists to develop ZnO in the field of science and technology. In addition, ZnO is lower in cost and is environmental friendly as compared to other metal oxides [2]. Normally, ZnO is studied in nanoscale; this is probably due to the fact that the high surface area to mass ratio of nanoparticles could enhance the adsorption of organic pollutants on the surface of particles as compared to the bulk materials [1].

However, undoped ZnO nanoparticles have certain limitation on light absorption catalytic activity. It was revealed that ZnO has alarge band gap energy of about 3.3 eV which can only absorb light within UV region. In addition, the fast recombination rate of photogenerated electron-hole pairs will also contribute to the limitation of photocatalytic activity. Thus, in order to enhance the optical, magnetic, and electrical properties of ZnO, the transition metal-doped ZnO nanoparticles have been introduced. The modification of ZnO nanoparticles with impurity incorporation leads to possible application in UV optoelectronic and spin electronics [3]. Among the transition elements, Mn shows the maximum magnetic behaviors with electron effective mass ~$0.3m_e$ (m_e = free electron mass); a doping of Mn into the ZnO semiconductor host lattice may result in large injected spins and carrier which make it suitable to be applied as diluted magnetic semiconductor (DMSs) [4].

Actually, the term "doped" is used to modify the optical or magnetic properties of the host by adding impurities ions against the host lattice. The doping with 3d metals such as Mn, Ni, Fe, Co, and Cr will increase the surface area and reduce the particle size of ZnO nanoparticles [5]. Mn is preferred for

Table 1: Amounts of reactant required to prepare nanoparticles with different manganese concentrations.

	Amounts added in mmol for mol% of $Zn(OAc)_2{\cdot}2H_2O$, $Mn(OAc)_2{\cdot}2H_2O$ and NaOH					
Chemicals	0	3	5	10	15	20
$Zn(OAc)_2{\cdot}2H_2O$	2.00	1.94	1.90	1.80	1.70	1.60
$Mn(OAc)_2{\cdot}4H_2O$	0.00	0.06	0.10	0.20	0.30	0.40
NaOH	2.00	2.00	2.00	2.00	2.00	2.00

the doping of ZnO due to the fact that the d electron of Mn at t_{2g} level can easily overlap with the ZnO's valence bond as compared with other transition elements. There are various studies which showed, that Mn-doped semiconductors have influenced the physical, chemical, and structural properties of undoped ZnO nanoparticles. For example, the optical properties of undoped ZnO nanoparticles especially on the tuning of the band gap can be greatly improved at the nanoscale by optimum content of Mn doping [6, 7].

Currently, the synthesis of Mn-doped ZnO nanoparticles can be through various types of methods such as wet-chemical, sol-gel, coprecipitate, solid-thermal, and spray pyrolysis. In order to enhance the optical properties and obtain a small particle size, a search for alternative synthesis methods for efficiency Mn doping with ZnO nanoparticles has become the major interest of studies. The purpose of this work was to synthesize band gap energy tunable of Mn-doped ZnO nanoparticles with high surface area for better photocatalytic performance using coprecipitation method. Zinc acetate ($Zn(ac)_2{\cdot}2H_2O$) and manganese acetate ($Mn(ac)_2{\cdot}4H_2O$) act as precursors and absolute ethanol was used as a solvent to synthesis Mn-doped ZnO nanoparticles. Basically, the synthesis of electrostatically stable Mn-doped ZnO nanoparticles was performed in an alcoholic solution in order to avoid the formation of ZnOH [8].

2. Experimental

2.1. Materials. All the chemicals used were analytical grade and were used in this experiment without further purification. The chemicals used were zinc acetate dehydrate ($Zn(OAc)_2{\cdot}2H_2O$), >99.5%, from Fluka), manganese acetate tetrahydrate, ($Mn(OAc)_2{\cdot}4H_2O$, >98%), sodium hydroxide (NaOH, 98%), and absolute ethanol (C_2H_5OH, >99%).

2.2. Synthesis Procedures of Mn-Doped ZnO Nanoparticles. Mn-doped ZnO nanoparticle was prepared by using sol-gel method [8]. Mn-doped ZnO nanoparticles were synthesized by the reaction of Zn^{2+}, Mn^{2+}, and OH^- in an alcoholic medium (ethanol). For 5 mol% of Mn-doped ZnO nanoparticles, there were generally three solutions that needed to be prepared. The first solution contained 20 mM of zinc acetate dehydrate ($Zn(ac)_2{\cdot}2H_2O$) in 10 mL of ethanol. The second solution consisted of 1.0 mM of manganese acetate tetrahydrate ($Mn(ac)_2{\cdot}4H_2O$) in 10 mL of ethanol. Then, the next solution consisted of 20 mM of NaOH in 10 mL of ethanol. These three solutions at first were heated to 50°C. After heating, zinc acetate solution was poured into round bottom flask and then manganese acetate solution was added to it. Zinc acetate and manganese acetate solution was again heated to 80°C with constant stirring for 30 minutes. Then, NaOH solution was added dropwise into the solution containing $Zn(ac)_2{\cdot}2H_2O$ and $Mn(ac)_2{\cdot}4H_2O$ along with reflux. The solutions were again heated to 60–65°C with magnetic stirring for 2 h. After this, the solution was cooled to room temperature. The precipitate was formed and was washed several times with distilled water and then followed by ethanol. The purpose of washing precipitate with ethanol was to remove the unwanted salt and impurities.

To investigate the effect of different concentrations of Mn dopant ions on the physical, chemical, and optical properties of Mn-doped ZnO nanoparticles, the same procedures as stated above were carried out for 3 mol%, 10 mol%, 15 mol%, and 20 mol% of Mn-doped ZnO nanoparticles. Table 1 below shows the amount of reactant required to prepare nanoparticles with different manganese concentrations.

2.3. Characterization. The effects of Mn/ZnO on the composition, morphology, and optical properties of Mn-doped ZnO nanoparticles were determined by various techniques. Elemental and chemical composition of Mn-doped ZnO nanoparticles were carried out using a Scanning Electron Microscope-Energy Dispersive X-ray (SEM-EDX). Surface morphologies of Mn-doped ZnO nanoparticles were carried out using a Scanning Electron Microscope (SEM). The SEM images are shown in the magnification of 10,000. FTIR analysis was performed using a FTIR spectroscopy Perkin Elmer spectrum GX model to obtain information about the chemical bonding and molecular structure in a sample. The optical absorption spectra of Mn-doped ZnO nanoparticles were carried out using a UV-visible Spectrophotometer operating at a wavelength range of 300 nm to 500 nm. Fluorescence spectrophotometer, CARY Eclipse, and Varian model were used to investigate the effect of different Mn-doped contents on the optical emission properties of Mn-doped ZnO nanoparticles.

3. Results and Discussion

3.1. Morphological Studies. The influence of different percentage of Mn (3, 5, 10, 15, and 20 mol%) on the surface morphologies of Mn-doped ZnO nanoparticles was studied by SEM which is shown in Figure 1. It can be seen that as the percentage of Mn doped increases, the grain size of the ZnO nanoparticles is also increasing (Table 2). From the SEM images, it can be seen that with above 15 mol%, the agglomeration increases. This may probably be related to the kinetic equilibrium process where the high concentration of Mn

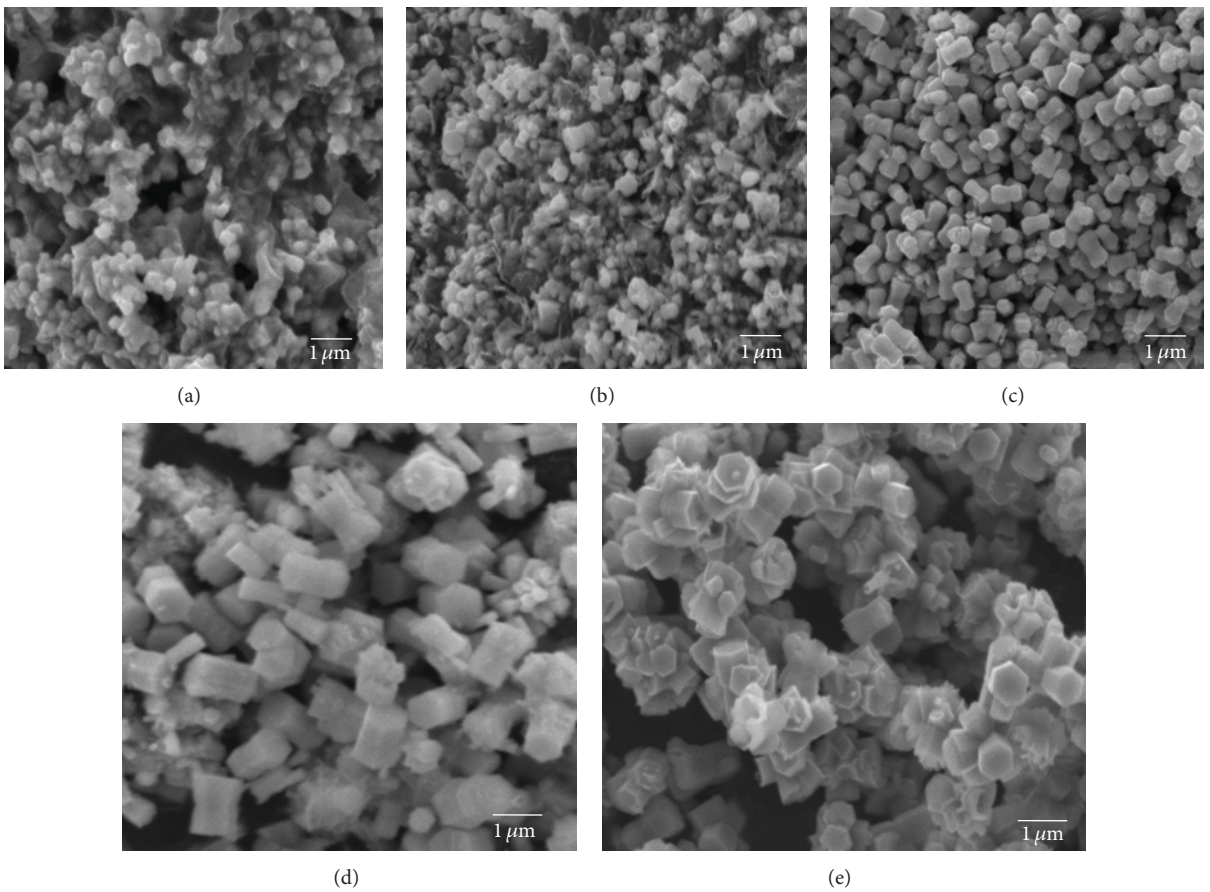

Figure 1: SEM images of Mn-doped ZnO nanoparticles with (a) 3 mol%, (b) 5 mol%, (c) 10 mol%, (d) 15 mol%, and (e) 20 mol%.

Table 2: The mean size obtained from different percentage of Mn doping in ZnO nanoparticles.

Manganese dopant concentration (mol%)	Mean particle size (nm)
3	157
5	187
10	245
15	432
20	509

dopants could be nucleated with oxygen ions by itself and form bigger particles. Hence, it could be difficult for the Mn to be incorporated into ZnO lattice in higher concentration. As a conclusion, a lower dopant concentration of Mn-doped ZnO nanoparticles showed lower agglomeration and well-ordered and small particles size distribution than the higher Mn dopant concentration [9].

3.2. Elemental and Chemical Composition Analysis. Figure 2 shows the EDX spectrum of 3 mol%, 5 mol%, 10 mol%, 15 mol%, and 20 mol% of Mn-doped ZnO nanoparticles. From the EDX spectrum, it can be seen that the amount of Mn element in the samples increased depending on the increasing Mn incorporation in the ZnO nanoparticles. The area of the corresponding spectral K lines gives the quantitative results of the Mn/Zn ratio [10]. The elemental analysis for O, Mn, and Zn for each sample (3 mol%, 5 mol%, 10 mol%, 15 mol%, and 20 mol%) was shown in Table 3.

3.3. FTIR Analysis. Various peaks corresponding to the main absorption bands can be seen from the FTIR spectrum on Figure 3. The broad absorption peak around 3376 cm^{-1}, 3377 cm^{-1}, and 3378 cm^{-1} represents the O–H stretching of the hydroxyl group. The peak around 2900 cm^{-1} was due to C–H (acetate) stretching [11]. Two absorption peaks are observed between 1650 and 1400 cm^{-1}, corresponding to the asymmetric and symmetric stretching of the carboxyl group (C=O).

From the studies, the stretching mode of undoped ZnO is at 431 cm^{-1}. In this work, for $Zn_{1-x}Mn_xO$ (x = 0.03, 0.05, 0.10, 0.15, and 0.20), the values of absorption were found to be blueshifted at 443, 450, 462, 470, and 481 cm^{-1}, respectively. Undoubtedly, this can prove that the Zn–O–Zn network was perturbed by the presence of Mn in its environment with the change in the peak position of the ZnO absorption bands [12].

3.4. Optical Studies. In this work, we obtained the wavelength for undoped ZnO and 3 mol%, 5 mol%, 10 mol%, and 15 mol% Mn-doped ZnO nanoparticles. It was observed that

Table 3: Mass % of O, Mn, and Zn as determined by EDX analysis.

Element	Mass %				
	3 mol%	5 mol%	10 mol%	15 mol%	20 mol%
O	23.48	33.73	7.60	43.31	53.34
Mn	3.26	4.66	9.51	15.23	20.97
Zn	73.25	61.62	82.89	41.46	25.69

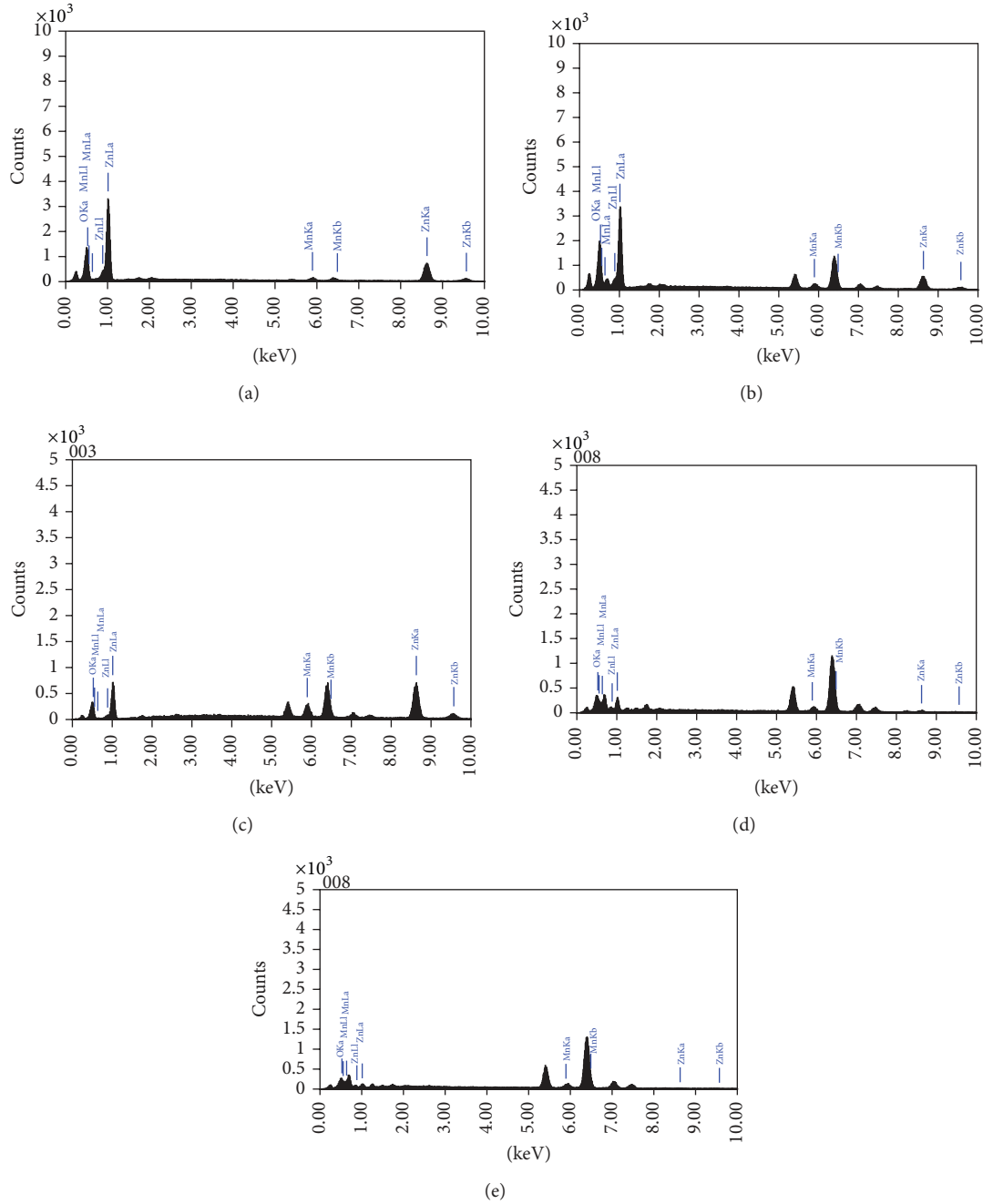

Figure 2: EDX spectrum of Mn-doped ZnO nanoparticles with (a) 3 mol%, (b) 5 mol%, (c) 10 mol%, (d) 15 mol%, and (e) 20 mol%.

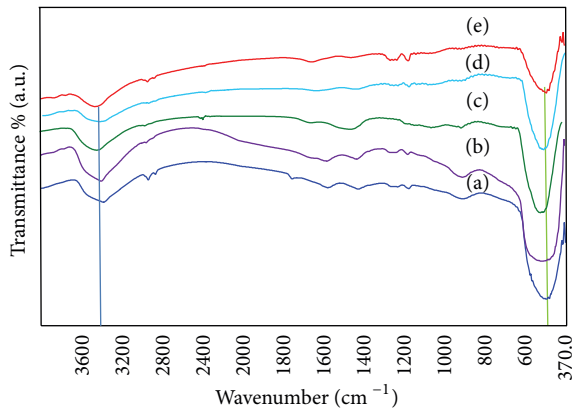

FIGURE 3: FTIR spectrum of Mn-doped ZnO nanoparticles with (a) 3 mol%, (b) 5 mol%, (c) 10 mol%, (d) 15 mol%, and (e) 20 mol% of Mn dopant concentrations.

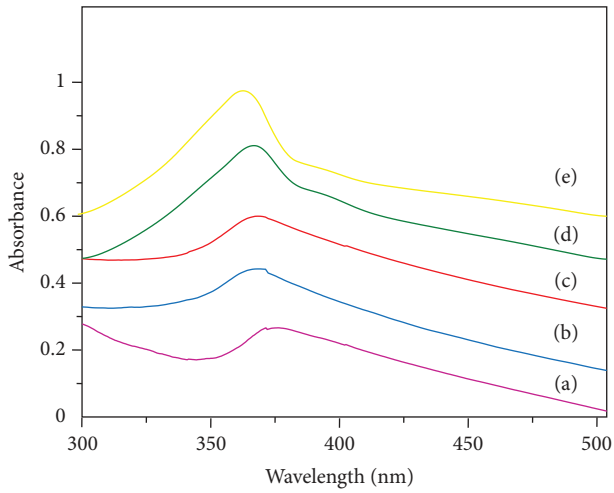

FIGURE 4: Absorbance spectrum of Mn-doped ZnO nanoparticles with (a) pure ZnO, (b) 3 mol%, (c) 5 mol%, (d) 10 mol%, and (e) 15 mol%.

the absorption edges of undoped ZnO and 3 mol%, 5 mol%, 10 mol% and 15 mol% of Mn doping are 374.5, 370, 367, 365, and 362.5 nm as shown in Figure 4.

With the increasing of Mn concentration in ZnO nanoparticles, the position of the absorption spectra is shifted towards the lower wavelength side or known as blue-shifted which is correlated to the change in the optical band gap value. The band gap energy of undoped and Mn-doped ZnO nanoparticles could be determined using the following formula: $E_{bg} = hc/\lambda$, where E_{bg} is the band gap energy, h is Planck's constant (4.135667×10^{-15} eV s), c is the velocity of light (2.997924×10^{8} m/s), and λ is the absorption wavelength (nm) [11]. The value of the band gap obtained for undoped ZnO is 3.31 eV and it starts increasing for 3, 5, 10, and 15 mol% samples as 3.35, 3.38, 3.40, and 3.42 eV, respectively.

Generally, blueshifted in the band gap was due to Mn doping in ZnO nanoparticles with the replacement of Zn^{2+} ions in the ZnO lattice by Mn^{2+} ions. This indicates that the band gap of ZnO nanoparticles increases with the increasing doping concentration of Mn^{2+} ion. Furthermore, the blueshifted

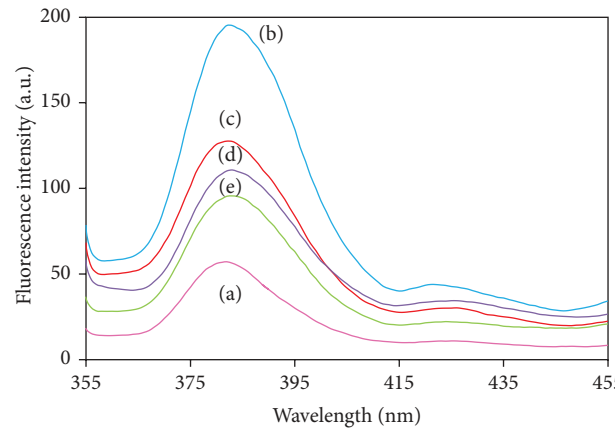

FIGURE 5: Fluorescence spectra of Mn-doped ZnO nanoparticles with (a) pure ZnO, (b) 3 mol%, (c) 5 mol%, (d) 10 mol%, and (e) 15 mol%.

in the band gap energy with increasing the amount of Mn doping concentration can be defined as the separation in energy between the top of the valence bond and the unoccupied energy states in the conduction band [13].

The fluorescence spectrum of undoped ZnO nanoparticles was taken into account for the comparison of fluorescence intensity between the undoped and Mn-doped ZnO nanoparticles. From the studies, it was known that ZnO tends to produce intrinsic defects such as interstitial zinc and oxygen vacancy and these defects will certainly affect the fluorescence behaviour of ZnO. The fluorescence emission peak shifts are found to be size dependent due to quantum size effect. The shift from the top of the valence band and the bottom of conduction band is contributed as a function of fluorescence emission peaks shift. Normally, it was indicated that a redshift of UV emission as the particle size increases [14]. The intrinsic luminescence properties of ZnO rely upon the concentration of Mn doping and thus the fluorescence intensity decreases with the increasing of Mn dopant concentration and the spectrum related to a Mn dopant concentration of 3 mol% shows the maximum of fluorescence intensity which is shown in Figure 5. The increase of fluorescence intensity indicates that the incorporation of Mn^{2+} ion into ZnO nanoparticles may suppress some nonradiative recombination of free excitation that is near band-edge emission. Moreover, on doping with Mn, the surface traps are eventually quenched which is correlated to the reduction in the surface traps. Moreover, higher concentration of Mn may induce a high density of defects and thus reduces the intensity of emitted light [15].

4. Conclusion

Mn-doped ZnO nanoparticles have been successfully synthesized through coprecipitation method. The effects of manganese dopant concentrations (3 mol%, 5 mol%, 10 mol%, 15 mol%, and 20 mol%) on the composition, morphologies and optical properties of Mn-doped ZnO nanoparticles have been investigated through EDX, FTIR, SEM, UV-visible spectroscopy, and fluorescence spectra.

Conflict of Interests

The authors declare that they have no conflict of interests regarding the publication of this paper.

Acknowledgment

The authors would like to thank the University of Malaya for sponsoring this work under the University Malaya Research Grant (UMRG RP022-2012A) and the Bright Sparks Program.

References

[1] H. D. Raval and J. M. Gohil, "Nanotechnology in water treatment: an emerging trend," *International Journal of Nuclear Desalination*, vol. 4, no. 2, pp. 184–188, 2010.

[2] J. Iqbal, X. Liu, A. Majid, and R. Yu, "Synthesis and physical properties of Mn doped ZnO dilute magnetic semiconductor nanostructures," *Journal of Superconductivity and Novel Magnetism*, vol. 24, no. 1-2, pp. 699–704, 2011.

[3] L. W. Wang, Z. Xu, F. J. Zhang, S. L. Zhao, and L. F. Lu, "Structure, optical, and magnetic properties of Mn-doped ZnO films prepared by sputtering," *International Journal of Minerals, Metallurgy and Materials*, vol. 17, no. 4, pp. 475–480, 2010.

[4] W. Shi-Wei, Z. Ming-Yuan, Z. Min et al., "Effects of pulsed magnetic field on Mn-doped ZnO diluted magnetic semiconductor prepared by hydrothermal method," *Acta Physica Sinica*, vol. 61, no. 19, Article ID 198103, 2012.

[5] X. X. Yan and G. Y. Xu, "Effect of sintering atmosphere on the electrical and optical properties of (ZnO)1-x(MnO2)x NTCR ceramics," *Physica B*, vol. 404, no. 16, pp. 2377–2381, 2009.

[6] Y. Abdollahi, A. Abdullah, Z. Zainal, and N. Yusof, "Synthesis and characterization of Manganese doped ZnO nanoparticles," *International Journal of Basic and Applied Sciences*, vol. 11, no. 4, pp. 62–69, 2011.

[7] B. Soni, M. P. Deshpande, S. Bhatt, N. Garg, N. Pandya, and S. H. Chaki, "Influence of Mn doping on optical properties of ZnO nanoparticles synthesized by microwave irradiation," *Journal of Optics*, vol. 42, no. 4, pp. 328–334, 2013.

[8] O. D. Jayakumar, H. G. Salunke, R. M. Kadam, M. Mohapatra, G. Yaswant, and S. K. Kulshreshtha, "Magnetism in Mn-doped ZnO nanoparticles prepared by a co-precipitation method," *Nanotechnology*, vol. 17, no. 5, pp. 1278–1285, 2006.

[9] M. Yang, Z. X. Guo, K. H. Qiu et al., "Synthesis and characterization of Mn-doped ZnO column arrays," *Applied Surface Science*, vol. 256, no. 13, pp. 4201–4205, 2010.

[10] S. Senthilkumaar, K. Rajendran, S. Banerjee, T. K. Chini, and V. Sengodan, "Influence of Mn doping on the microstructure and optical property of ZnO," *Materials Science in Semiconductor Processing*, vol. 11, no. 1, pp. 6–12, 2008.

[11] M. Y. Hao, S. Y. Lou, S. M. Zhou, R. J. Yuan, G. Y. Zhu, and N. Li, "Structural, optical, and magnetic studies of manganese-doped zinc oxide hierarchical microspheres by self-assembly of nanoparticles," *Nanoscale Research Letters*, vol. 7, no. 100, pp. 1–13, 2012.

[12] D. Wu, Z. Huang, G. Yin et al., "Preparation, structure and properties of Mn-doped ZnO rod arrays," *CrystEngComm*, vol. 12, no. 1, pp. 192–198, 2010.

[13] R. Viswanatha, S. Sapra, S. S. Gupta et al., "Synthesis and characterization of Mn-doped ZnO nanocrystals," *Journal of Physical Chemistry B*, vol. 108, no. 20, pp. 6303–6310, 2004.

[14] L. Irimpan, V. P. N. Nampoori, P. Radhakrishnan, A. Deepthy, and B. Krishnan, "Size dependent fluorescence spectroscopy of nanocolloids of ZnO," *Journal of Applied Physics*, vol. 102, no. 6, Article ID 063524, 2007.

[15] F. I. Ezema and U. O. A. Nwankwo, "Effect of concentration of Mn dopant ions on the structural and optical properties of zinc oxide crystals," *Digest Journal of Nanomaterials and Biostructures*, vol. 6, no. 1, pp. 271–278, 2011.