Optical and Photocatalytic Properties of ZnS:Mn Nanocrystals∗

Tran Thi Quynh Hoa,† Nguyen Hoang Nam, Ta Dinh Canh, and Nguyen Ngoc Long
Faculty of Physics, Hanoi University of Science, 334 Nguyen Trsimilar, Thanh Xuan, Hanoi, Vietnam

Hoang Manh Ha
In-service Faculty, Hanoi Architectural University, Km 10 Nguyen Trí, Thanh Xuan, Hanoi, Vietnam

(Received 25 November 2009; Accepted 17 March 2011; Published 27 December 2011)

The colloidal ZnS:Mn nanoparticles were obtained by using thermochemical method with the reaction duration varied from 1 h to 7 h. The bandgap of the ZnS:Mn nanocrystals increases from 3.75 eV to 4.06 eV with decreasing particle size from 5.8 nm to 2.4 nm, respectively. At room temperature, the ZnS:Mn nanoparticles exhibit orange-red emission due to the $^{4}T_1(T_{2}) \rightarrow ^{6}A_{1}(S)$ transition within the 3$d^5$ configuration of Mn$^{2+}$ ions inside the ZnS host. The orange-red photoluminescence can be excited at energies corresponding to the Mn$^{2+}$ ion own excited states. The $^{6}A_{1}(S) \rightarrow ^{4}E_{2}(P)$, $^{6}A_{1}(S) \rightarrow ^{4}T_{1}(P)$, $^{6}A_{1}(S) \rightarrow ^{4}E_{2}(G)$, $^{4}A_{1}(G)$, $^{6}A_{1}(S) \rightarrow ^{4}T_{1}(G)$, and $^{6}A_{1}(S) \rightarrow ^{4}T_{2}(G)$ absorption transitions have been observed in the photoluminescence excitation spectra. Photocatalytic properties of the samples have been investigated via absorption spectra of methyl orange (MO) in present of ZnS:Mn nanoparticles. The photo-degradation of MO obeys the pseudo-first-order kinetics law. The reaction rate constant k for MO degradation was 0.0065 min$^{-1}$. [DOI: 10.1380/ejssnt.2011.516]

Keywords: Nanoparticles; ZnS: Mn; Photoluminescence; Photocatalysis; Thermochemical method

I. INTRODUCTION

ZnS nanocrystals have been studied intensively because of variety application in the field of emission devices, optical coatings, electrooptic modulators, optical sensor, and photocatalysis [1, 2]. In particular, ZnS:Mn nanocrystals can yield both a higher luminescent efficiency and a lifetime shorter in comparison with the bulk of ZnS:Mn, thus they are important materials in technology of plasma displays, laser [3] and biosensor [4]. These unique properties of ZnS:Mn nanocrystals have attracted much interest for both basic research and application purposes. There are many methods available for synthesis ZnS:Mn nanocrystals, such as reverse micelle [4], chemical [5], solid state diffusion at high temperature [6], thermochemical [7], hydrothermal [8] and sonochemical [9] methods. In this paper, the colloidal ZnS:Mn nanoparticles have been prepared by thermochemical method with different reaction conditions.

II. EXPERIMENTAL

For synthesis of ZnS:Mn nanoparticles, zinc acetate, sodium thiosulfate and manganese acetate were dissolved separately in de-ionized water and stirred at room temperature for 30 min. ZnS:Mn samples were prepared by 2 steps. In the first step, 120 ml of mixed solution containing 0.1 M zinc acetate, 1 M sodium thiosulfate, and 1 μM manganese acetate was prepared. The solution was put in reaction bath, heated at 90 °C for an hour and continuously stirred during the synthesis process. In the second step of the synthesis, 70 ml of 1.1 M thiglycerc (TG) was rapidly added to the solution while the heating and stirring process was continued. Soon after adding TG, the solution became more white sludgy during synthesis process. The change in colour and state of the solution indicates formation of colloidal nanocrystals. We have synthesized the ZnS:Mn samples with different reaction time. After various intervals of time, an amount of 30 ml of the colloidal solution was taken out from the reaction solution. The reaction time was chosen to be 55, 65, 70, 75, 90, 120, 240, and 420 min for synthesis of samples 1, 2, 3, 4, 5, 6, 7, and 8, respectively.

The colloidal solutions were then centrifuged, had the supernatant layer poured off, washed with double distilled water. The washing procedure was repeated ten times to remove impurities in the samples. The colloidal aqueous samples were dried at 60 °C in air for 12 h. The final products have been received in two kinds: powder (samples 1, 2, 3, 4, and 5 with reaction time in the range from 55 min to 90 min) and dried colloid like gel (samples 6, 7, and 8 with reaction time in the range from 120 min to 420 min).

The photocatalytic activities of ZnS:Mn nanocrystals (sample 8) have been evaluated by the degradation of methyl orange (MO) solution under 254 nm radiation from low - pressure Mercury lamp. In the experiment, 100 ml of 3.55 μM MO aqueous solution was transferred into the glass vessel and 3 ml of ZnS:Mn colloidal solution was added to form the suspensions. Then the suspensions were stirred magnetically for 1 h in a dark condition in order to establish an adsorption - desorption equilibrium. The glass vessel then was placed under the 254 nm radiation. During the experiment every 3 ml of suspension was taken through a pipette at different interval of time and then was centrifuged. The clear part of centrifuged suspension will be taken as a sample for absorption measurement and the residue will be restored for cyclical experiments.

The crystal structure of the prepared ZnS:Mn samples was analyzed by X-ray diffraction using a Brucker D5005 diffractometer. The microstructures and morphology of

∗This paper was presented at the International Workshop on Advanced Materials and Nanotechnology 2009 (IWAMN2009), Hanoi University of Science, VNU, Hanoi, Vietnam, 24-25 November, 2009.
†Corresponding author: tranthiquynhhoa@gmail.com

ISSN 1348-0391 © 2011 The Surface Science Society of Japan (http://www.sssj.org/ejssnt) 516
the samples were characterized by transmission electron microscopy (JEOL JEM 1010). The absorption spectra were obtained by a Shimadzu UV 2450 PC spectrometer. The photoluminescence (PL) and photoluminescence excitation (PLE) spectra were recorded by using a FL3-22 Jobin Yvon Spex spectrofluorometer.

III. RESULTS AND DISCUSSION

Figure 1 shows typical TEM images of the ZnS:Mn nanoparticles. As can be seen from the images, the ZnS:Mn grains are agglomerated in colloids, the average sizes are about 3 nm. The XRD patterns of the ZnS:Mn products are presented in the Fig. 2. The patterns show the position of various diffraction peaks at $2\theta$ values of 28.7°, 47.7°, and 56.4°, corresponding to the diffraction planes (111), (220), and (311), respectively. The peaks were perfectly indexed to the cubic zincblende phase of ZnS.

The information on the crystalline size has been obtained from the following Debye - Scherrer relations [10]:

$$L = \frac{0.9\lambda}{\beta \cos \theta}$$

where $\beta$ is the full width at half maximum (FWHM) in radians of the diffraction peaks, $\theta$ is the Bragg’s diffraction angle and $\lambda$ is the wavelength for the K$_{\alpha 1}$ component of the employed copper radiation (1.54056 Å). The particle sizes are estimated to be 2.42 nm, 2.60 nm, 2.72 nm, 2.94 nm, 3.10 nm, 3.28 nm, and 3.55 nm for samples 2, 3, 4, 5, 6, 7, and 8, respectively. It indicated that the longer reactive times are, the bigger particle sizes become. Thus, by controlling the reaction time the particle size can be varied.

ZnS is a direct bandgap semiconductor. The relation between the absorption coefficients ($a$) and the incident photon energy ($h\nu$) for the case of allowed direct transition is given by equation [11]:

$$a h\nu = A(h\nu - E_g)^{1/2}$$

where $A$ is a constant and $E_g$ is the bandgap of the material. Figure 3 shows the photon energy dependence of $(a h\nu)^2$ for the ZnS:Mn nanoparticles prepared with various reaction times. The plots of $(a h\nu)^2$ vs $h\nu$ allow to estimate the bandgap of the samples.

The bandgap values of the ZnS:Mn nanoparticles synthesized for different reaction times are presented in table I. The blue-shift of the absorption band edge with respect to that of the bulk samples (3.72 eV) [12] was attributed to the quantum size effect. From the blue-shift of the band edge ($\Delta E$), the crystalline radius could be determined using the relation given below [13]:

$$\Delta E = E_{g(np)} - E_{g(bulk)} = \frac{\hbar^2}{8\mu R^2} - k \frac{1.8e^2}{\varepsilon r}$$

http://www.sssj.org/ejssnt (J-Stage: http://www.jstage.jst.go.jp/browse/ejssnt/)
TABLE I: Particle size L calculated from the XRD data (column 3) and particle radius r calculated by using formula (3) (column 6) for samples 1, 2, 3, 4, 5, 6, 7, and 8.

| Sample | Reaction time t (min) | Particle size L (nm) | $E_g$(np) (eV) | $\Delta E$ (eV) | Particle radius r (nm) |
|--------|-----------------------|----------------------|---------------|----------------|------------------------|
| 1      | 55                    | 4.06                 | 0.34          | 2.44           |
| 2      | 65                    | 4.05                 | 0.33          | 2.47           |
| 3      | 70                    | 4.02                 | 0.30          | 2.57           |
| 4      | 75                    | 4.01                 | 0.29          | 2.61           |
| 5      | 90                    | 3.99                 | 0.27          | 2.69           |
| 6      | 120                   | 3.96                 | 0.24          | 2.82           |
| 7      | 240                   | 3.94                 | 0.27          | 2.92           |
| 8      | 420                   | 3.75                 | 0.03          | 5.83           |

where $E_g$(np) and $E_g$(bulk) are the bandgaps of nanoparticles and bulk materials, respectively; $h$ is the Planck constant; $k$ is a constant depending on unit system; $\mu = m^*_e m^*_h/(m^*_e + m^*_h)$ is the reduced electron-hole pair effective mass and $m^*_e$ and $m^*_h$ are the effective masses of electrons and holes, respectively; $\varepsilon$ is the dielectric constant of the material. For the ZnS nanoparticles, we have taken $m^*_e = 0.34m_e$, $m^*_h = 0.23m_e$, and $\varepsilon = 8.76$ [14], $m_e$ is the free electron mass.

Using the mentioned Eq. (3), the particle sizes were determined to be 2.44 nm, 2.47 nm, 2.57 nm, 2.61 nm, 2.69 nm, 2.82 nm, 2.92 nm and 5.83 nm for the samples 1, 2, 3, 4, 5, 6, 7, and 8, respectively (see Table I). The nanoparticle size increases with increasing the reaction time. These sizes are larger than that calculated from the XRD spectra. The bandgap value was decreased as the particle size increased. It is in agreement with the XRD analysis results.

Photoluminescence property of the samples was investigated at room temperature. Emission spectra under the 330 nm (3.76 eV) excitation wavelength are shown in Fig. 4. The spectra of samples exhibit two broad emission bands, one is a blue emission band at about 450 nm and another is an orange band at about 597 nm. For sample 1, which received before addition of TG, the PL spectra show an emission band peaked at 450 nm and a weak orange band peaked at 597 nm. For sample 2, which received at once after addition of TG, the emission band at 597 nm became stronger; meanwhile the 450 nm band became remarkably weak. The longer reactive times are, the stronger the orange emission becomes. It is indicated that the TG acted as a passivation agent to enhance photoluminescence intensity.

A similar phenomenon is also obtained for PL spectra excited by the 362 nm (3.43 eV) wavelength. In the spectra, apart from the 450 nm and 597 nm emission bands, a shoulder 640 nm emission band was observed as well. Thus, the PL spectra are an overlap of three emission bands centered at 450 nm, 597 nm, and 640 nm. The typical multiplet Gauss fitting of the spectra shows three components as can be seen from Fig. 5.

The red emission at 640 nm (1.94 eV) maybe is originated from the deep defects such as the interstitial Zn, S
For investigation of the luminescence mechanism causing the orange emission, photoluminescence excitation spectra monitored at wavelength of 597 nm have been recorded. In the PLE spectra (Fig. 6), there have been observed some absorption peaks. In the range of 375-600 nm, one shoulder at 396 nm, three peaks at 430 nm, 466 nm, and 496 nm and another shoulder at 530 nm were observed. The Mn$^{2+}$ photoluminescence can be excited at energies corresponding to the Mn$^{2+}$ ion own excited states. Compared to the results of [6], these peaks may be assigned to the $^{6}A_{1}(^{6}S)$→$^{4}E_{2}(^{4}P)$; $^{6}A_{1}(^{6}S)$→$^{4}T_{2}(^{4}P)$; $^{6}A_{1}(^{6}S)$→$^{4}E(^{4}G)$; $^{4}A_{1}(^{4}G)$; $^{6}A_{1}(^{6}S)$→$^{4}T_{2}(^{4}G)$, and $^{6}A_{1}(^{6}S)$→$^{4}T_{1}(^{4}G)$ absorption transitions within the $3d^{5}$ configuration of Mn$^{2+}$ ions.

The photocatalytic activities of ZnS:Mn have been investigated. The results showed that the irradiation time and the particle size of the ZnS:Mn catalysts have obvious influence on the degradation of the reactive MO.

The color-change of the MO solution mixed with the ZnS:Mn nanoparticles of sample 8 as a function of UV irradiation duration is shown in Fig. 7. It was observed that the MO solution with the intense orange color was gradually changed to colorless MO solution with increasing UV irradiation time. The same phenomenon also occurred for the MO solution mixed with the ZnS:Mn nanoparticles of all other samples. In addition, we revealed that the smaller particle size is, the faster photodegradation process occurs.

Figure 8 shows typical absorption spectra of MO solution in presence of ZnS:Mn nanoparticles of sample 8 under exposure to UV light with various durations. The intensity of major absorption band decreases gradually when UV irradiation duration increases. It means that the concentration of MO decreased with increasing irradiation time.

ZnS:Mn nanoparticles of sample 8 as a function of UV irradiation duration is shown in Fig. 8. It was observed that the MO solution with the intense orange color was gradually changed to colorless MO solution with increasing UV irradiation time. The same phenomenon also occurred for the MO solution mixed with the ZnS:Mn nanoparticles of all other samples. In addition, we revealed that the smaller particle size is, the faster photodegradation process occurs.

The mechanism of photocatalytic process has been discussed previously [17–19]. In general, it can be described as follows:

$$\text{ZnS:Mn} + h\nu \rightarrow e^{-} + h^{+} \quad (4)$$
$$h^{+} + \text{H}_2\text{O} \rightarrow \text{H}^{+} + \text{OH}^{-} \quad (5)$$
$$h^{+} + \text{OH}^{-} \rightarrow \text{OH}^{•} \quad (6)$$
$$e^{-} + \text{O}_2 \rightarrow \text{O}_2^{−} \quad (7)$$
$$\text{O}_2^{−} + \text{H}^{+} \rightarrow \text{HO}_2 \quad (8)$$
$$(\text{OH}^{•}, \text{O}_2^{−}, \text{HO}_2) + \text{MO} \rightarrow \text{Degradation products} \quad (9)$$

When the aqueous ZnS:Mn suspension is irradiated by the light with energy greater than the ZnS:Mn bangap energy, the conductive band electrons ($e^{-}$) and valence band holes ($h^{+}$) are generated (reaction 4). By tunnel effect the electrons and holes can move to the surface of the ZnS:Mn...
particles, react and generate some radicals such as OH\(^{-}\), O\(_2\)\(^{-}\) and HO\(_2\) adsorbed at the surface of the ZnS:Mn particles (reactions 5-8). The formed radicals are very strong oxidizing agents. MO can be completely photo-degraded into \(\text{H}_2\text{O}, \text{CO}_2\) and mineral acids (reaction 9).

The photodegradation obeys the pseudo first order kinetics law, which is expressed by the formula [17]:

\[
\ln(C/C_0) = kt
\]

(10)

where \(C_0\) is the initial concentration, \(C\) is the concentration after time \(t\) of the MO degradation and \(k\) is the first order rate constant.

As shown in Fig. 9, the rate of MO degradation in the presence of various ZnS:Mn is determined via the first order rate constant. The reaction rate constant \(k\) is 0.0065 min\(^{-1}\).

IV. CONCLUSION

ZnS:Mn nanoparticles have been synthesized by thermochemical method. The XRD spectra revealed that the synthesized particles have cubic zinclabe structure. The ZnS grains are agglomerated in colloids, the average sizes are about 3 nm. The longer reactive times are, the bigger particle sizes become. The bandgap value increases from 3.75 eV to 4.06 eV with decreasing the nanoparticle size. The TG is represented as passivation agent to enhance photoluminescence intensity. The orange emission is due to the localized \(4\text{T}_1(4\text{G})\) \(\rightarrow\) \(6\text{A}_1(4\text{S})\) transition within the \(3\text{d}^6\) configuration of Mn\(^{2+}\) ions inside ZnS host. The absorption transitions \(6\text{A}_1(6\text{S})\rightarrow 4\text{E}_2(4\text{P})\); \(6\text{A}_1(6\text{S})\rightarrow 4\text{T}_2(4\text{P})\); \(6\text{A}_1(6\text{S})\rightarrow 4\text{E}(4\text{G})\), \(4\text{A}_1(4\text{G})\); \(6\text{A}_1(6\text{S})\rightarrow 4\text{T}_2(4\text{G})\), and \(6\text{A}_1(6\text{S})\rightarrow 4\text{T}_1(4\text{G})\) have been observed in the photoluminescent excitation spectra. The photocatalytic activity of the prepared ZnS:Mn was demonstrated by decomposing MO under UV light radiation. The photodegradation rate constant \(k\) is 0.0065 min\(^{-1}\).

Acknowledgments

This work is financially supported by Ministry of Science and Technology of Vietnam (Contract No 38/355/2008/HD-NDT for Task of Protocol with Israel and Project No 103.02.51.09 from NAFOSTED). Authors of this paper would like to express their sincere gratitude to the Center for Materials Science (CMS), Faculty of Physics, Hanoi University of Science, Vietnam National University for permission to use equipment.

[1] S. Biswas, S. Kar, and S. Chaudhuri, J. Phys. Chem. B 109, 17526 (2005).
[2] H. C. Warad, S. C. Ghosh, B. Hemtanon, C. Thanachayanont, and J. Datta, Sci. Technol. Adv. Mater. 6, 296 (2005).
[3] R. N. Bhargava, J. Lumin. 70, 85 (1996).
[4] E. Mohagheghpour, M. Rabiee, F. Moztarzadeh, M. Tahriri, M. Jafarbeglou, D. Bizar, and H. Esfami, Mater. Sci. Eng. C 29, 1842 (2009).
[5] H. Yang, J. Zhao, L. Song, L. Shen, Z. Wang, L. Wang, and D. Zhang, Mater. Lett. 57, 2287 (2003).
[6] W. Chen, R. Sammyaiken, Y. Huang, J.-O. Malm, R. Wallenberg, J.-O. Bovin, V. Zwiller, and N. A. Kotov, J. Appl. Phys. 89, 1120 (2001).
[7] G. Hajisalem, M. Marandi, N. Taghavinia, and M. Houshiar, Nanotechnology 20, 095706 (2009).
[8] S. Biswas and S. Kar, Nanotechnology 19, 045710 (2008).
[9] H. Wang, J.-R. Zhang, and J.-J. Zhu, J. Cryst. Growth 246, 161 (2002).
[10] B. E. Warren, X-ray Diffraction (Dover publications, Inc., New York, 1990), p. 253.