

A simple one Step Thermochemical Approach for Synthesis of ZnS:Mn Nanocrystals (NCs)

Mehdi Molaei, Ahmad Lotfiani, Fatemeh Karimimaskon, Masoud Karimipour, and Mohammdd Khanzadeh

Abstract—In this work we have synthesized ZnS:Mn nanocrystals (NCs) using a simple one step thermochemical method. $\text{Zn}(\text{NO}_3)_2$ and $\text{Na}_2\text{S}_2\text{O}_3$ were used as the precursors and $\text{Mn}(\text{NO}_3)_2$ was the source of impurity. Thioglycolic acid (TGA) was used as the capping agent and the catalyst of the reaction. The structure and optical property of the NCs were characterized by means of X-ray diffraction (XRD), HRTEM, UV-visible optical spectroscopy and photoluminescence (PL). X-ray diffraction (XRD) and transmission electron microscopy (TEM) analyses demonstrated cubic phase ZnS:Mn NCs with an average size around 3 nm. Synthesized NCs exhibited band gap of about 4 eV. Photoluminescence spectra showed a yellow-orange emission with a peak located at 585 nm, demonstrating the Mn incorporation inside the ZnS particles.

Index Terms—ZnS:Mn, nanocrystals (NCs), photoluminescence

I. INTRODUCTION

During recent years semiconductor nanocrystals (NCs) have been a subject of extensive interest because of their extensive application such as light emitting devices, optical sensitizers and photovoltaic devices applications [1-4]. Among the semiconductor NCs, ZnS is an important semiconductor material with interesting

physical properties and wide band-gap energy of 3.7 eV at 300 K. Luminescence properties of ZnS can be controlled using various doping impurity such as Mn, Ni, Cu etc [5-7]. Because of these properties ZnS and doped-ZnS are good candidates for application in optical sensors and light emitting devices [8, 9]. Different transition metal doped ZnS NCs such as ZnS:Mn [5], ZnS:Cu [6], ZnS:Ni [7] and ZnS:Cr [10], were investigated during recent years. Recently, ZnS and doped ZnS NCs have been synthesized by various methods, including solid-state reaction [11], sol-gel process [12], hydrothermal method [13], organic metallic method [14], micro-emulsion technique [15], and reverse micelle method [16]. However, these synthesis approaches are relatively more complicated and some of these methods require longer processing times, high temperatures and use of non-aqueous solvents. In this work, we have reported a simple one step and rapid thermochemical method for synthesis of ZnS:Mn NCs and investigated the photoluminescence properties of synthesized NCs. $\text{Zn}(\text{NO}_3)_2$ and $\text{Na}_2\text{S}_2\text{O}_3$ were used as the precursors and $\text{Mn}(\text{NO}_3)_2$ was used as impurity source. This method is based on the heat sensitivity of $\text{Na}_2\text{S}_2\text{O}_3$. $\text{Na}_2\text{S}_2\text{O}_3$ is a heat sensitive material releasing S species and free electrons needed for the ZnS formation reaction.

II. EXPERIMENTAL DETAILS

1. Synthesis of ZnS:Mn NCs

The synthesis of doped ZnS NCs was performed using $\text{Zn}(\text{NO}_3)_2$ and $\text{Na}_2\text{S}_2\text{O}_3$ as the precursors and $\text{Mn}(\text{NO}_3)_2$

as the source of the impurity. TGA was used as a capping agent as well as the catalyst of the reaction. $\text{Na}_2\text{S}_2\text{O}_3$ is a UV and heat sensitive material releasing S species and free electrons needed for the ZnS formation reaction [7]. In a typical synthesis a 100 cc solution of $\text{Zn}(\text{NO}_3)_2$, $\text{Mn}(\text{NO}_3)_2$, $\text{Na}_2\text{S}_2\text{O}_3$ and TGA was prepared in a way that the final concentrations were 20, 0.2, 50 and 15 mM, respectively. The solution was purged with argon for 15 min and then put in a water bath at 80°C for 20 minutes only. The solution was continuously stirred during the synthesis process.

2. Characterization

X-ray diffraction (XRD) was performed on the centrifuged and extracted particles using an Advanced d8 Bruker system. Optical transmission was measured using a T70/T80 UV-visible (UV-vis) spectrometer. Photoluminescence (PL) measurements were performed using a Varian system. TEM image was recorded using a 200 kV JEOL 2010 system.

III. RESULTS AND DISCUSSION

1. XRD and TEM Analysis

Fig. 1 shows the XRD pattern of the ZnS:Mn synthesized NCs. The positions of the three main peaks correspond to (111), (220) and (311) planes of cubic zinc blende structure, which matches with the standard card (JCPDS No. 05-0566) [5, 7]. There is not any observable impurity phase in the spectra, indicating the formation of pure cubic phase of ZnS only. The broadening of diffraction peaks indicates the formation of NCs. Using the full width at half maximum (FWHM) of the first main XRD peak and Debye-Scherrer's formula, crystallite size of ZnS:Mn is estimated to be about 2.7 nm.

Figs. 2(a) and (b) are two HRTEM images of the synthesized NCs. The particles are round in shape and NCs with a size of about 3 nm can be seen in two images which is consistent with the obtained sizes from XRD pattern.

2. UV-Vis and Photoluminescence Analysis

Fig. 3(a) indicates the absorption spectra of the

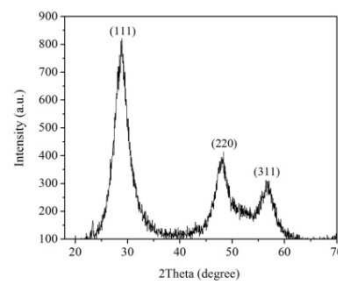


Fig. 1. XRD pattern of the synthesized ZnS:Mn NCs.

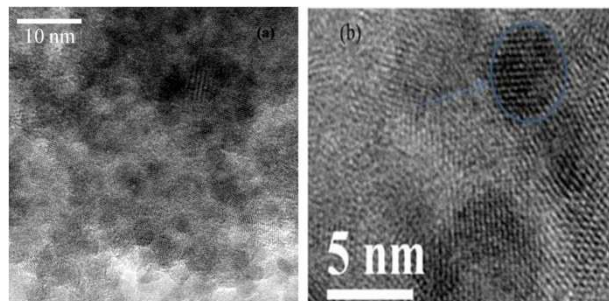


Fig. 2. Two typical HRTEM images (a) and (b) of the synthesized ZnS:Mn (Mn/Zn=1%) NCs.

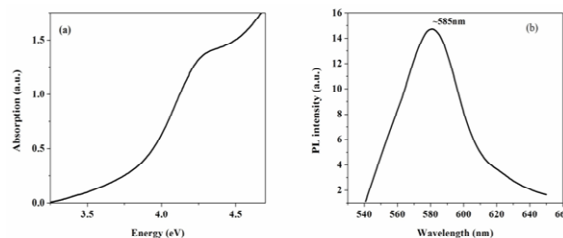


Fig. 3. Absorption (a) and PL spectra (b) of the ZnS:Mn (Mn/Zn=1%) NCs.

synthesized ZnS:Mn. There is a sharp band edge located at around 4 eV which shows the ZnS NCs band gap. The particle size is obtained to be about 3.2 nm from tight binding method [17]. Fig. 3(b) demonstrates the PL spectra of the synthesized NCs. There is a PL peak located at about 585 nm. Fig. 4 shows the energy diagram for ZnS:Mn systems, according to this diagram, the yellow/orange (585 nm) emission is related to ${}^4\text{T}_1 \rightarrow {}^6\text{A}_1$ transitions in Mn^{2+} ions inside the ZnS host [5]. The PL peak indicates the effective incorporation of Mn ions inside the ZnS NCs.

Fig. 5 shows the absorption (a) and PL spectra (b) of the ZnS:Mn NCs synthesized with different concentration of the Mn impurity. As seen in Fig. 5(a), the absorption edge has no change with respect to the doping concentrations. Mn:Zn=0 ratio does not result in

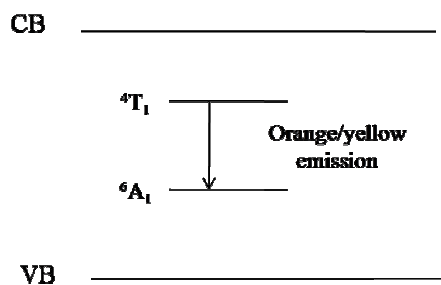


Fig. 4. energy diagram of the Mn doped ZnS.

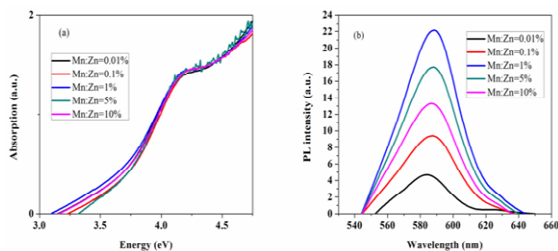


Fig. 5. Absorption (a) and PL spectra (b) of ZnS:Mn NCs synthesized with different concentration of the Mn impurity.

luminescent NCs. PL intensity is ascending for up to Mn:Zn=1 concentration and is descending for higher values. Many researchers found concentration quenching for the photoluminescence intensity of Mn^{2+} doped ZnS NCs. Maity and Chattopadhyay [18] found an optimal Mn^{2+} concentration of 0.07%. Khosravi et al. [19] observed a maximum luminescence at a doping concentration of 0.12 wt%. Leeb et al. [20] reported an optimal Mn^{2+} concentration of 1%. Peng et al. [21] obtained a maximum luminescence at a doping concentration of 1.03%, and Xiao and Xiao [22] showed a maximum luminescence at a doping concentration of 1.5%. In all of these reported works, luminescence quenching is attributed to the predomination of the Mn–Mn dipolar interactions. In the present work, concentration quenching was also observed. In doped ZnS NCs it will be expected that the Mn impurity ion occupy the Zn site. Therefore increase of the Mn impurity concentration up to 1% will increase the radiative states density which it will results in increase of the PL intensity. If Mn^{2+} concentration increases more than 1%, the Mn^{2+} emission would decrease which suggests that Mn–Mn dipolar interactions may be predominant in the prepared solution. Above 1% concentration, the isolated Mn^{2+} ion may also stay at the surface or interstitial position of the crystallites with

octahedral symmetry and these do not favor radiative transition.

IV. CONCLUSION

ZnS:Mn (NCs) were synthesized using a new simple one step thermochemical method. X-ray diffraction (XRD) and transmission electron microscopy (TEM) analyses demonstrated cubic phase ZnS:Mn NCs with an average size around 3 nm. Photoluminescence spectra showed a yellow-orange emission with a peak located at about 585 nm, demonstrating the Mn incorporation inside the ZnS particles. By increasing Mn:Zn ratio, the PL intensity increases and indicates a maximum for Mn:Zn=1%.

REFERENCES

- [1] P. O. Anikeeva, J. E. Halpert, M. G. Bawendi and V. Bulovi, *Nano Lett.* 7 (2007) 2196.
- [2] A. P. Alivisato, *Science* 271 (1996) 933.
- [3] M. Molaei, M. Marandi, E. Saievar-Iranizad, N. Taghavinia, B. Liu, H. D. Sun and X.W. Sun, *J. Lumin.* 132 (2012) 467.
- [4] M. Molaei, E. Saievar Iranizad, Z. Dehghani, N. Taghavinia and M. H. Majlesara, *Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry* 41 (2011).
- [5] G. Hajisalem, M. Marandi, N. Taghavinia and M. Houshiar, *Nanotechnology* 20 (2009) 095706.
- [6] A. Tiwari, S. A. Khan, R. S. Kher, *J. Lumin.* 132 (2012) 1564.
- [7] M. Molaei, *J. Lumin.* 136 (2013) 38.
- [8] R. Mach, G. Muller, *J. Cryst. Growth* 86 (1988) 866.
- [9] T. Yamaguchi, Y. Yamamoto, T. Tanaka, A. Yoshida, *Thin Solid Films* 344 (1999) 516
- [10] D. Amaranatha Reddy, G. Murali, B. Poornaprakash, R. P. Vijayalakshmi, B. K. Reddy, *Solid State Commun.* 152 (2012) 596.
- [11] V. Stanic, T.H. Etsell, A.C. Pierre, *Mater. Lett.* 31 (1997) 35.
- [12] T.A. Gupton, C.L. Czekai, C.G. Pantano, *J. Non-Cryst. Solids* 121 (1990) 7.
- [13] T. Hanaoka, T. Taqo, M. Kishida, *Bull. Chem. Soc. Jpn.* 74 (2001) 1349.

- [14] R.N. Bhargava, D. Gallagher, X. Hong, A. Nurmikko, Phys. Rev. Lett. 72 (1994) 416.
- [15] S.J. Xu, S.J. Chua, B. Liu, L.M. Gan, C.H. Chew, G.Q. Xu, Appl. Phys. Lett. 73 (1998) 478.
- [16] L. X. Cao, J. H. Zhang, S.L. Ren, S.H. Huang, Appl. Phys. Lett. 80 (2002) 4300.
- [17] P. E. Lippens and M. Lanno, Phys. Rev. B 39 (1989) 10935.
- [18] R. Maity, K. K. Chattopadhyay, Nanotechnology 15 (2004) 812.
- [19] A. A. Khosravi, M. Kundu, B. A. Kuruvilla, G. S. Shekhawat, R.P. Gupta, A. K. Sharma, P.D. Vyas, S.K. Kulkarni, Appl. Phys. Lett. 67 (1995) 2506.
- [20] J. Leeb, V. Gebhardt, G. Muller, D. Haarer, D. Su, M. McMahon, L. Spanhel, J. Phys. Chem. B 103 (1999) 7839
- [21] W.Q. Peng, S.C. Qu, G.W. Cong, X.Q. Zhang, Z.G. Wang, J. Cryst. Growth 282 (2005) 179.
- [22] Q. Xiao, C. Xiao, J. Appl. Surf. Sci. 254 (2008) 6432



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