American Journal of Engineering Research (AJER)
e-ISSN: 2320-0847 p-ISSN : 2320-0936
Volume-7, Issue-6, pp-27-32
www.ajer.org
Research Paper Open Access

Study Of Single-Step Synthesis Of Hyperbranced Highly Luminescence Doped Znse:Mn, Znse:Mn/Zns Quantum Dots And Their Interactions With Acid Amine

Xuan Truong Mai[1], Diem Thi Bui[2], Duykhanh Pham[1],Thanhthao Bui[3],Thanh Mien Nguyen[4], Jinwoo Oh[4], Ngoc Quyen Tran[1,5], Bichthi Luong[1]*
[1]*Institute of Applied Materials Science, Vietnam Academy of Science and Technology, Vietnam*
[2]*Industrial University of Ho Chi Minh City, Vietnam*
[3]*Faculty of Chemical Engineering, Ho Chi Minh City University of Technology, VNU-HCM, Vietnam*
[4]*Department of Nanoenergy Engineering, Pusan National University, Busan 609-735, South Korea*
[5]*Institute of Research and Development, Duy Tan University, Da Nang City 550000, Vietnam*
Corresponding Author: Xuan Truong Mai

ABSTRACT : *The water-soluble ZnSe:Mn corecapped with MPA, MUA, starch were synthesized respectively and ZnSe:Mn/ZnS core-shell capped with PVA quantum dots (QDs) was also produced. Herein, we report the interaction of obtained quantum dots with acid amin (Lysine). It was found that QDs effectively changes the fluorescence of acid amin that was surface coating. After acid amin was added, the QDs PL of the (MPA)-coated ZnSe:Mn, (Starch)-coated ZnSe:Mn increased dramatically in response to µM concentrations acid amin, when (MUA)-coated ZnSe:Mn, (PVA)-coated ZnSe:Mn effectively quenched.*
KEYWORDS *-core quantum dots,Core-shell quantum dots, Quantum dot-amine interaction, quantum dots based on zinc quantum dots-lysine.*

Date of Submission: 19-05-2018 Date of acceptance: 04-06-2018

I INTRODUCTION

Colloidal luminescent semiconductor quantum dots (QDs) are of considerable interest in the biological and medical disciplines, due to their promising applications in bio-imaging and bio-sensing among others[1, 2, 3, 4]. For example, highly fluorescent QDs could be prepared by pyrolyzingorgano-metallic reagents at high synthesis temperature in organic solvents. Inhighly fluorescent QDs could be prepared by pyrolyzingorgano-metallic reagents at high synthesis temperature in organic solvents[2,5,6]. This utilizes high boiling point solvents and high temperature (typically 200–350^{o}C). On the other hand, organo-metallic compounds are not only harmful and toxic, but also are more expensive. Direct synthesis of II–VI semiconductor quantum dots, such as CdSe, CdTe, CdHgTe, and ZnSe, in aqueous medium using stabilizing agents as starch, thiol,PVAcan provide an important alternative to the previously described high temperature protocols[7, 8, 9, 10]. Each method provides advantages and disadvantages, such that the synthetic method can be chosen depending on the application requirements. Overall, these nanocrystals have their high specific surface area and the deficiency in surface atomic coordination, the luminous efficiency of these QDs is significantly lower than other kinds of nanocrystals.

Doping with atomic impurities is an efficient way to generate luminescent QDs, due to their strong dopant emission. To date, colloidal QDs have successfully been doped with transition metals (such as Fe, Ni, Mn, Cu) and lanthanides (such as Eu, Er, Tm, Tb) to alter their electronic, optical or magnetic properties. Mn^{2+}-doped semiconductors are widely used in many photoluminescence and electroluminescent applications[5]. The availability of luminescent colloidal nanocrystals (NCs) of these materials expanded their use to bioimaging and sensing, and solar energy, among other applications[11].The nature of the Mn^{2+} dopants can provide a probe of local environment, elucidating NC structural information via their optical and magnetic properties. Applications involving Mn^{2+}phosphorescence involve doping of wide bandgap semiconductors [12]. The fixed $^{4}T_{1}$ energy level of the Mn^{2+} provides a trap for energy absorbed by the NC. This energy is released radiatively as an orange

luminescence. This is only observed when the conduction band energy level is above the energy of the $Mn^{2+4}T_1$, and thus frequently the zinc chalcogenides are employed as host materials.

Here, we synthesis ZnSe:Mn and ZnSe:Mn/ZnS QDs with different capping molecules such as mercaptopropionic acid (MPA), 11-mercaptoundecanoic acid (MUA), starch and polyninylalcohol (PVA). The produced quantum dots were attached with acid amine in order to survey the compatibility and change of photoluminescent property in order to apply in biosensor fabrication.

II EXPERIMENTAL SECTION

2.1. Materials

All the chemicals are of analytical grade, purchased from Sigma-Aldrich, and were used without further purification. Manganese(II) acetate ($Mn(OAc)_2$) (Mn (CH3COO)2.4H2O, 99.99%), zinc acetate ($Zn(OAc)_2$) (Zn (CH3COO)$_2$.2H2O, 99.99%) and sodium sulfide (Na_2S), 3-mercaptopropionic acid (MPA, 99+%), sodiumborohydride ($NaBH_4$, 96%), selenium powder (99.5%), 2-propanol (HPLC grade). Water (deionized water-DI water) used in all synthesis was high purity grade with a conductivity of 18.2 MU cm^{-1}. Synthesis of ZnSe:Mn and ZnSe:Mn/ZnS QDs a literature synthetic method of NaHSe solution that mixed with Zn^{2+} ionic solution to form ZnSe core QDs at the first step was used as previous report [8].

2.2. ZnSe:Mn

The precursor of Zn^{2+} ionic solution for ZnSe core formation was prepared by dissolution 10 ml of zinc acetate 0.1 M, 5 ml of manganese acetate 0,01 M in 90 ml of water, and 40 ml of MPA (starch, PVA, MUA) 0.1 M in three-neck flask, then the pH of this system was adjusted to pH ¼ 3 using NaOH 2 M with vigorous stirring. This three-neck flask was degassed by N2 bubble in 30 minutes, and then the NaHSe solution was injected into the Zn^{2+} precursor solution at room temperature under N_2. The system was heated to 70^{o}C and refluxed for 3 hours to optimize the refluxing time of the first ZnSe:Mn core growth step. The flask system was cooled down to room temperature to terminate reaction and prepared for further measurement or kept on stirring for the second ZnS growth step. The as-prepared NCs solution was purified by centrifugation and decantation with 2-propanol.

2.3. ZnSe:Mn/ZnS

At the second step ZnS shell coating onto ZnSe core by following process [8]. The previous three-flask reaction system was cooled to room temperature, then mixture of 8,7 ml of zinc acetate was drop-wised at one drop per second into flask reaction. And the temperature was raised to 80.0 °C, then the pH of reaction system was adjusted to 11.1 by NaOH 2 M to form majority S^{2-} anions in solution after 8.7 ml of Na_2S 0.1 M was injected slowly for ZnSe:Mn/ZnS core/ shell QDs formation. The reaction flask was stirred for one and half hours to get the faint yellow emission visible under UV light with 365 nm wavelength then it was cooled to room temperature and prepared for further measurement.

The obtained suspension was concentrated to one-tenth of the original volume, and then the QDs were precipitated in 2-propanol, washed and collected via centrifugation and decantation, finally dried in a vacuum. The obtained powder was used for characterization.

This synthetic method was briefly mentioned in previous research[8].

2.4. Interaction with acid amine

To demonstrate the utility of these NCs for biological sensing, the NCs were transferred to aqueous solution and add acid amine. Briefly, 0,01g of dry quantum dots (QDs) was solubilized in 10 ml of bidistilled water. The solutions were shaken for 30 min and measure a PL spectrum. After, acid amine has add to solutions and record the changes of PL spectrum[13, 14].

III RESULTS AND DISCUSSION

3.1. Structure and morphology

The crystal structure of the ZnSe core and ZnSe@ZnS core-shell NCs were analysed.

According to the IR results, surfactants are linked to QDs at the MPA and 11-MUA via thiol group which is the disappearance of the SH group by binding to QDs, whilePVAand starch are the substitutions of the OH group at about 3400.

The XRD profile of ZnSe quantum dots comprised of the typical signature of cubic zinc blende (JCPDS File No: 32-0483), which normally broadens due to finite crystallite size. The diffractive peaks were located at 27.40, 45.950, and 54.30 corresponding to the crystallographic planes (111), (220), and (311) of ZnSe. Moreover, from the XRD pattern, it was demonstrated that ZnS shells epitaxially grew on the surface of the ZnSe core rather than as a simple combination

TEM images show that (Figure 1) the obtained products are shaped crystalline and sized around 8 to 10 nm

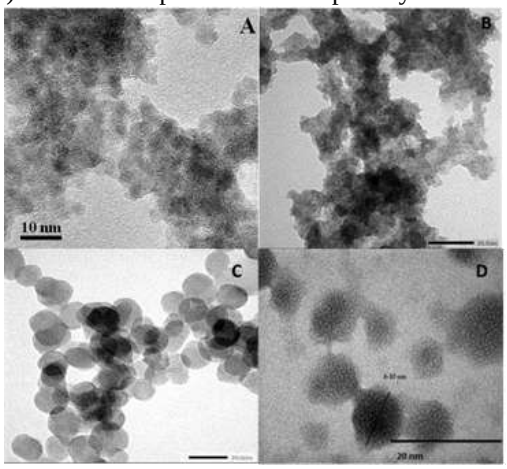

Figure 1. TEM image of QDs a) MPA ZnSe:Mnb) MUA ZnSe:Mn
c) Starch ZnSe:Mn, d)PVAZnSe:Mn/ZnS

3.2. Effect of QDs on acid amine absorption spectra

The interaction between QDs and amino acids was probed by UV-vis absorbance spectroscopy. NCs were exposed to UV before and after reacting with amino acids for 5 minutes. The results shown in Figures 2 a) and b) show that the samples have a constant absorption when added with amino acids, which indicates that the amount of energy that quantum dot is supplied is the same.

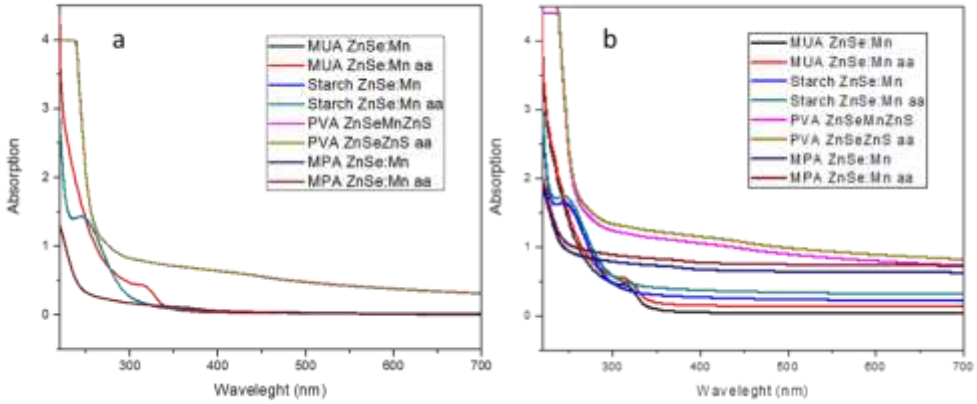

Figure 2.a) The UV spectra of ZnSe:Mnquantum dots after addition of acid amine b) The UV spectra of ZnSe:Mnquantum dots after addition of acid amine separately

3.3. Fluorescence quenching mechanism

The ZnSe / ZnS: X quantum dots show changes in luminous intensity when added with amino acids. The intensity can be varied to 35.92% as inPVAZnSe:Mn/ZnS in Figure 3 c namely the luminous intensity decreases by 35.92%.

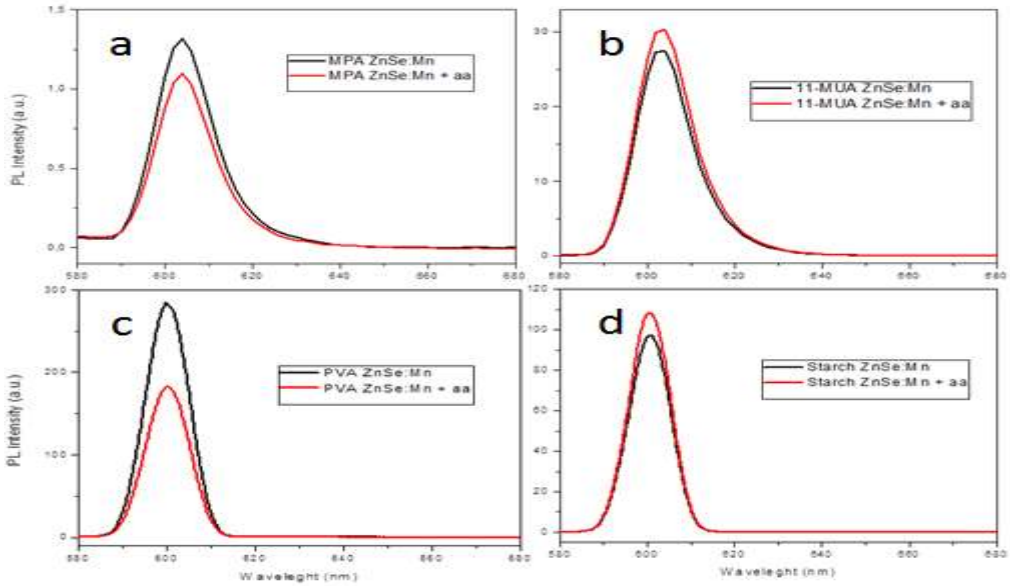

Figure 3.The PL spectrum of quantum dots by addition of amino acid
a) MPA-ZnSe:Mn b) MUA-ZnSe:Mn c) PVA-ZnSe:Mn/ZnS d) Starch-ZnSe:Mn

In the MPA system of Figure 3a,ZnSe: Mn is also reduced by 16.59%. The intensity of this change is due to the influence of electrons in the nanoparticles attached to amino acids. The binding of the amino acid group to the luminescent nanoparticle via the MPA molecule formed the imidation group (-CO-NH) of Figure 4 a), which draws electrons according to Lewis acid properties, which reduces the number of electrons in the whole system. This leads to a reduction in the number of electrons in the excited state, thus reducing the number of electrons moving from the excited state to the lowest energy level of the forbidden zone, resulting in reduced light output of whole system.

Figure 3 b) shows that after binding to amino acids via the 11-MUA bridge, the luminous intensity increased to 10.13% despite the formation of the imidazole removal group (CO-NH) Figure 4 a), this was The reason is that due to the long carbon cycle of the 11-MUA (10Carbons) molecules compared to the MPA (2Carbons), the effect of electrons on the long-chain of electrons is greater than that of the imidating electron impinges. The amount of charge for the luminescence nanoparticle system is linked to the 11-MUA amino acid. The final result is increased luminous intensity.

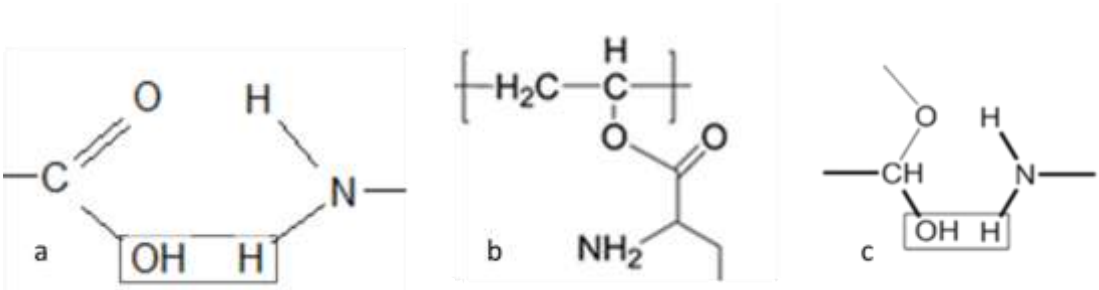

Figure 4. The ester linkage created creates a pathway for electrons from quantum dot througha) mecato acid, b) PVA, c) starch and amino acids

The luminescence intensity was significantly reduced by 35.92% after the amino acid bonding via thePVAbridge Figure 8 is the polymer circuit. Figure 3 c) shows this reduction. This is also explained by the loss of electrons in the luminescence nanoparticles and amino acids through thePVAbridge because polymers are bulky circuits that interfere with the charge space that moves into the system. This spatial effect of thePVA branches makes the intensity of light emission decrease, which is a good signal for the application of optical-chemical sensors.

Figure 3 d shows the increase in luminous intensity when amino acids are added. Because of the bonding between the groups -OH and -NH2 of the amino acid and the stabilizer on the surface of the quantum dot, the new CHO-NH bonds appear in Figure 4 c), from quantum dot to amino acid. Due to the long-chain

structure of the starch that prevails over the OH electron withdrawals, this stabilizer increases the amount of charge transferred to the system. The optical strength of the boost system is 11.53%.

From the above survey results, in order to further evaluate the probability of luminescence nanoparticles for amino acid, I chose ZnSe: Mn starch for further investigation. This product has high luminous intensity and luminosity is enhanced when added with amino acids.

Table 1 shows that each quantum dot gives a different signal when attached to an amino acid. Based on this feature we can build a biological sensor.

Table 1.the effect of capping agent on PL intensity after acid amine addition

Electron effect	Capping agent	% PL intensity
Acceptor	MPA	reducing 16.59%
Donor	11-MUA	raising 10.13%
Spacing effect	PVA	reducing 35,92%
Spacing–donor – acceptor	Starch	raising 11,53%

As shown in Figure 5, when the amount of amino acid added to more than 150 µl, the PL intensity does not change much (256.9 - 260.3 - 260.1). The relatively linear level of amino acid is lower, but it should be investigated further at this concentration.

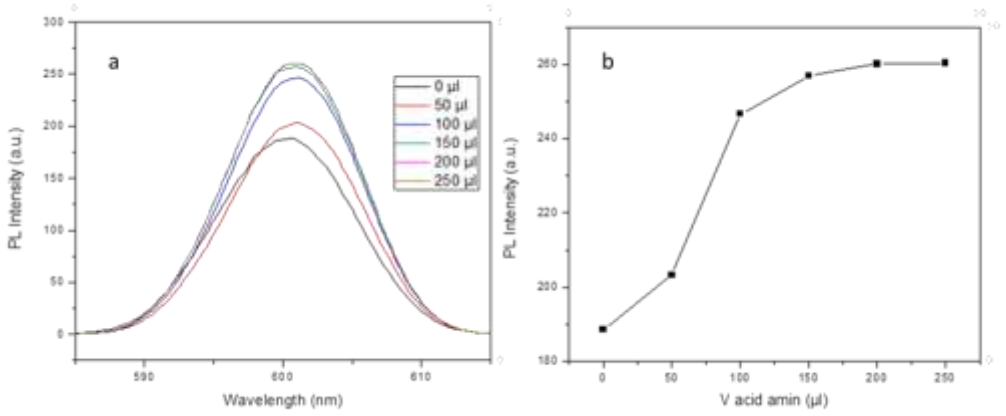

Figure 5.a) The PL spectrum of ZnSe:Mn(3%)-starch quantum dots when added with amino acid and b) the plot values according to Table 1

Figure 5 b) shows the luminous intensity of ZnSe: Mn synthesized with starch changed as the concentration of amino acid increased. We find that the graph is relatively linear in the range of 0-150µl and 100-250µl, which is capable of constructing a baseline for use in analyzing the concentration of the substance.

IV CONCLUSION

Although the energy supplied to quantum dots is constant for each type (no change in UV spectra), the luminous intensity of each quantum dot has a very different signal from table 1, and the change in signal intensity at a concentration of 11. This is promising for the production of both qualitative and quantitative sensors.

ACKNOWLEDGEMENTS

We sincerely thank the Department of Science and Technology of Ho Chi Minh City for funding this research project and the Ho Chi Minh City University of Industry have facilitated our completion research.

REFERENCES

[1]. A.V. Kir'yanov, N.N. Il'ichev, E.S. Gulyamova, A.S. Nasibov, P.V. Shapkin, Nonlinear Change in Refractive Index and Transmission Coefficient of ZnSe: Fe2+ at Long-Pulse 2.94-µm Excitation, *Optics and Photonics Journal, 5*, 2015, 15.

[2]. T.T.Q. Hoa, N.N. Long, V.T.H. Hanh, V.D. Chinh, P.T. Nga, Luminescent ZnS: Mn/thioglycerol and ZnS: Mn/ZnS core/shell nanocrystals: Synthesis and characterization, *Optical Materials, 35*, 2012, 136-140.

[3]. Z. Chen, D. Wu, Colloidal ZnSe quantum dot as pH probes for study of enzyme reaction kinetics by fluorescence spectroscopic technique, *Colloids and Surfaces A: Physicochemical and Engineering Aspects, 414*, 2012, 174-179.

[4]. S.J. Rosenthal, J.C. Chang, O. Kovtun, J.R. McBride, I.D. Tomlinson, Biocompatible quantum dots for biological applications, *Chemistry & biology, 18*, 2011, 10-24.

[5]. V. Wood, J.E. Halpert, M.J. Panzer, M.G. Bawendi, V. Bulovic, Alternating current driven electroluminescence from ZnSe/ZnS: Mn/ZnS nanocrystals, *Nano letters*, *9*, 2009, 2367-2371.
[6]. R. Thakar, Y. Chen, P.T. Snee, Efficient emission from core/(doped) shell nanoparticles: applications for chemical sensing, *Nano letters*, *7*, 2007, 3429-3432.
[7]. W.C. Law, K.T. Yong, I. Roy, H. Ding, R. Hu, W. Zhao, P.N. Prasad, Aqueous-Phase Synthesis of Highly Luminescent CdTe/ZnTe Core/Shell Quantum Dots Optimized for Targeted Bioimaging, *Small*, *5*, 2009, 1302-1310.
[8]. B.T. Luong, E. Hyeong, S. Ji, N. Kim, Green synthesis of highly UV-orange emitting ZnSe/ZnS: Mn/ZnS core/shell/shell nanocrystals by a three-step single flask method, *RSC Advances*, *2*, 2012, 12132-12135.
[9]. D. Zhu, X. Jiang, C. Zhao, X. Sun, J. Zhang, J.-J. Zhu, Green synthesis and potential application of low-toxic Mn: ZnSe/ZnS core/shell luminescent nanocrystals, *Chemical Communications*, *46*, 2010, 5226-5228.
[10]. Z. Fang, P. Wu, X. Zhong, Y.-J. Yang, Synthesis of highly luminescent Mn: ZnSe/ZnS nanocrystals in aqueous media, *Nanotechnology*, *21*, 2010, 305604.
[11]. S. Coe, W.-K. Woo, M. Bawendi, V. Bulović, Electroluminescence from single monolayers of nanocrystals in molecular organic devices, *Nature*, *420*, 2002, 800.
[12]. T. Kennedy, E. Glaser, P. Klein, R. Bhargava, Symmetry and electronic structure of the Mn impurity in ZnS nanocrystals, *Physical Review B*, *52*, 1995, R14356.
[13]. I.A. Mir, K. Rawat, H. Bohidar, Interaction of plasma proteins with ZnSe and ZnSe@ ZnS core-shell quantum dots, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, *520*, 2017, 131-137.
[14]. M.S. Yazdanparast, M.T. Webb, E.J. McLaurin, Single-step synthesis of hyperbranched, luminescent Mn 2+-doped ZnSe 1− x S x nanocrystals using dichalcogenide precursors, *Journal of Materials Chemistry C*, *4*, 2016, 6907-6913.

Xuan Truong Mai." Study Of Single-Step Synthesis Of Hyperbranced Highly Luminescence Doped Znse:Mn, Znse:Mn/Zns Quantum Dots And Their Interactions With Acid Amine."American Journal Of Engineering Research (AJER), Vol. 7, No. 6, 2018, Pp.27-32.