VNU Journal of Science: Mathematics – Physics, Vol. 31, No. 4 (2015) 32-38

Optical Properties of Zn-based Semiconductor Nanoparticles and Application in Two-barcode Encryption

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Received 01 August 2015
Revised 20 September 2015; Accepted 18 November 2015

Abstract: Mn-doped ZnS (ZnS/Mn) nanoparticles synthesized by sono-chemical co-precipitation are combined with ZnO nanoparticles synthesized by sol-gel method for application in two-barcode encryption. Nanoparticles are mixed together in different mass proportions of ZnO: ZnS/Mn respectively being 5: 1, 10: 1, 15: 1, 20: 1, 25: 1.30 : 1 and 35: 1, before being pressed in 1 cm diameter, 1 mm thick KBr pellets. The photoluminescence (PL) of the tablet shows that the mass proportion of two materials could be distinghuished by the proportion of the PL intensities at 515 nm and 600 nm, which promises potential manufacturing ability two-substant/two-barcode information storage systems for civil security applications.

Keywords: Photoluminescent encryption, Zn-based semiconductor, civil application.

1. Introduction

Recent years, semiconductor nanoparticles are interesting materials for biomedical applications such as cell imaging [1], drug delivery [2] or gene therapy [3], as well as applications in multipurpose encryption [4, 5] due to their optical properties. In application for encryption, polystyrene micro-beads that contain two types of CdSe/ZnS core-shell nanoparticles were created by inversed emulsion method [4, 5]. Under UV-light excitation, the micro-beads emit visible light with two distinghuished narrow peaks. The relative intensity of the two narrow peaks could be modified by controling the proportion of the two semiconductor core-shell particles under the synthesizing process. The material is comfortable to apply in multi-target cell imaging. Besides those applications, semiconductor nanoparticles are also used as optical encryption for civil security [6]. However, the manufaction of those nanoparticles requires critical laboratorial conditions, which raise the cost of comercial products to unreasonable level.

In this report, we use a simple process to fabricate ZnO and ZnS/Mn nanoparticles with high performance. Then, we use these zinc-base semiconductor nanoparticles to make a simple code system includes two substances, and assess the usability of the system for civil encryption.

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2. Experiment and method

2.1. Synthesis of ZnS/Mn nanoparticles

The nanoparticles are prepared by ultrasonic-assisted co-precipitation method. Briefly, 40 mL of 0.1 M Na_2S solution are wisedropped to 200 mL solution containing 2 mmol $Zn(NO_3)_2$, 180 µM $Mn(NO_3)_2$, 20 mg PVP and 20 mM SDS. During the addition of Na_2S, ultrasonic of power 0.2 kW and frequency 40 kHz is applied. A white colloid product that contains ZnS/Mn particles is centrifugated several times with 50% ethanol in order to wash all by-products.

X-ray diffraction (XRD), transmitted electron microscopic (TEM) imaging of the as-prepared particles is investigated.Fluorescent spectra of ZnS/Mn particles are observed under 335 nm excitation in 390 - 640 nm interval, while fluorescence excitation spectra are measured in 300 - 430 nm interval with the fluorescence wavelength of 590 nm.

2.2. Synthesis of ZnO nanoparticles

ZnO nanoparticles are synthesized by sol-gel method in 3 steps: gel creation, xerogel creation and annealing. In gel creation step, $Zn(NO_3)_2$ is mixed with citric acid (CA) with molar ratio of 1: 6 in aqueous solution. The solution is placed in an incubator at 80°C for 20h; yellow gel formation is created. In step 2, the gel system is dried at 200°C for 2h; grey spongy xerogel is formed. In the last step, the xerogel powder preliminary granulated before being annealed at 650°C for 4h. The final product is a white powder of ZnO nanoparticles.

X-ray diffraction (XRD), transmitted electron microscopic (TEM) imaging, scanning electron microscopic (SEM) image and energy dispersive X-ray (EDX) pattern of the as-prepared particles is investigated.

Fluorescent spectra of ZnO particles are observed under 360 nm excitation in 410 - 650 nm interval while fluorescence excitation spectra are measured in 280 – 450 nm interval with the fluorescence wavelength of 511 nm.

2.3. Application for optical 2-barcode system

ZnO and ZnS/Mn nanoparticles are mixed together in different mass ratios of ZnO:ZnS/Mn, which are 5: 1, 10: 1, 15: 1, 20: 1, 25: 1.30 : 1 and 35: 1. 20 mg of each mixture is pressed into KBr thin cylinder pellet. Fluorescent spectra of the pellet are investigated under 350 nm excitation.

3. Result and discussion

3.1. Structure and morphology

ZnS/Mn nanoparticles

X-ray diffraction parttern of ZnS/Mn nanoparticles is showed in Fig.1A. The observed peak positions coincide with the (111), (200) and (220) peaks of close-packed face central cubic JCP2

No. 05-0566 sphelartie ZnS. TEM image in Fig. 1B shows that the ZnS/Mn particles are formed with very small size of around 2 nm. This can be judged by the effect of surface active substances combined with the effect of the ultrasonic horn.

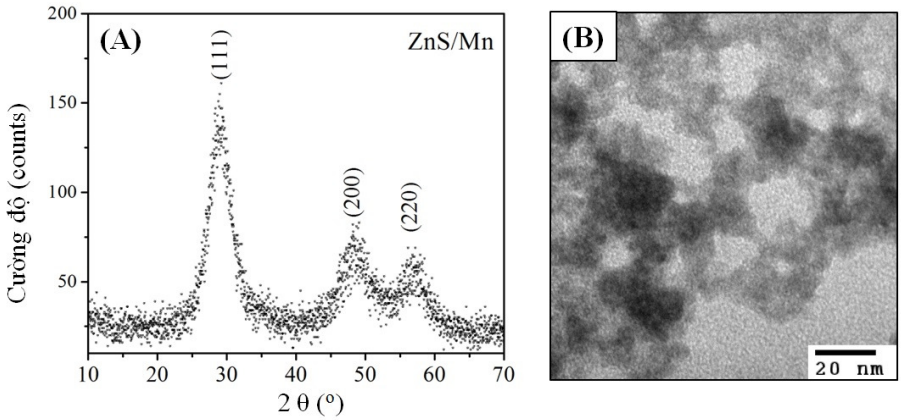

Figure 1. XRD parttern (A) and TEM image (B) of ZnS/Mn nanoparticles prepared by ultrasonic-assisted co-precipitation method.

ZnO nanoparticles

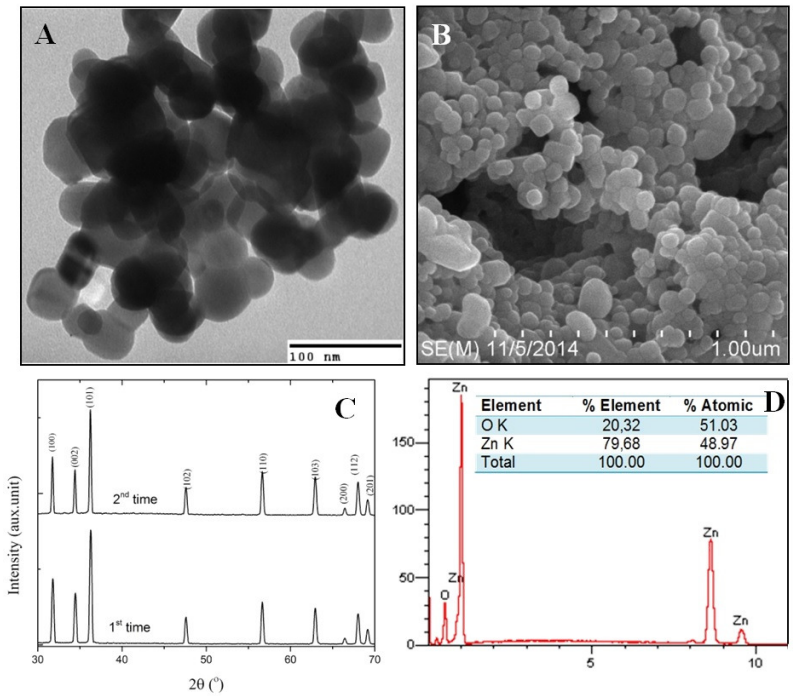

Figure 2. TEM image (A), SEM image (B), XRD (C) and EDX parttern (D) of ZnO nanoparticles prepared by sol-gel method.

Under the effect of high Citric acid concentration, ZnO nanoparticles have mostly homogeous sizes within 50-60 nm as shown by TEM image in Fig. 2A and SEM image in Fig 2B. It was discussed that when the CA:Metal ion ratio increases, there are more linkages between the metal ion with the organic molecules formulated in xerogel structure [7]. The metal ion – CA complex formation plays important roles not only as oxygen source but also as size controlling agent; more linkage increases the distance between the metal ions in the xerogel complex, hence decreases the size of the particles. Besides, annealing temperature also plays an important role in changing the particle size. At higher temperatures, the particles were aggregated into larger particles. However, at low temperature, the thermal energy is not enough to vaporize all residual carbon in the sample [8]. We have studied and showed that the optimumannealing temperature is between 650^{o}C and 700^{o}C.

Fig. 2C is the XRD pattern of the materials in two different synthesis times in order to check the reproducibility of the synthesizing process. Both products show hexagonal structure without any impurities. Besides, EDX spectrum in Fig. 2D affirms that the elemental proportion of Zn: O is 51:49 without any other unwanted elements.

3.2. Photoluminescence of the materials

Photoluminescent property of ZnS/Mn nanoparticles

Thephotoluminescence (PL) and excitation (PLE) of ZnS/Mn particles are investigated and the results are shown in Fig. 3. The presence of Mn^{2+} transition metal as doppant in the material creates a relatively high peak at 595 nm, which corresponds to energy difference of two energy states of Mn^{2+}, $^4T_1$ and $^6A_1$ [9]. The PLE (Fig.3A) spectrum shows a peak at 338 nm, of which the energy is close to the band gap of base crystal ZnS (3.54 eV for bulk material). Besides, there are two small peaks observed at 495 nm and 506 nm (Fig. 3A – inset). The energies of these peaks are close to the energies of $^4T_1$ and $^4T_2$ states of Mn^{2+}, which indicates the presence of Mn^{2+} in the materials.

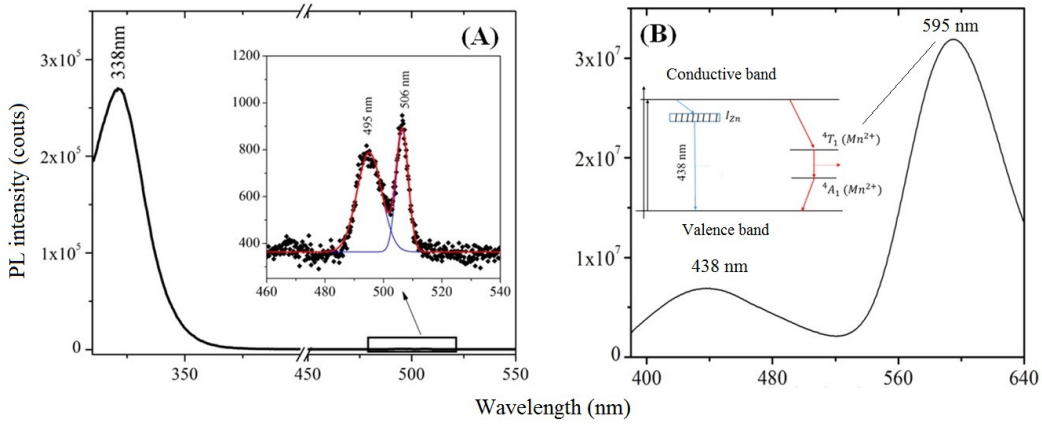

Figure 3. Photoluminescent excitation (PLE) spectrum (A) and photoluminescence (PL) spectrum (B) of ZnS/Mn nanoparticles.

Photoluminescent property of ZnO nanoparticles

PL and PLE spectra of ZnO materials are presented in Figure 4. In the PLE spectrum, there is one peak at 360 nm, which is close to the band gap of ZnO (3.37 eV for bulk materials). Light of the wavelength 360 nm was used as excitation source to collect PL spectrum. The PL spectrum of ZnO nanoparticles shows a peak at 511 nm, which could corespond to the ussual oxygen vacancy energy state of ZnO material. This result agrees with the EDX result, which showed that oxygen is slightly deficient in our samples (Zn:O = 51:49).

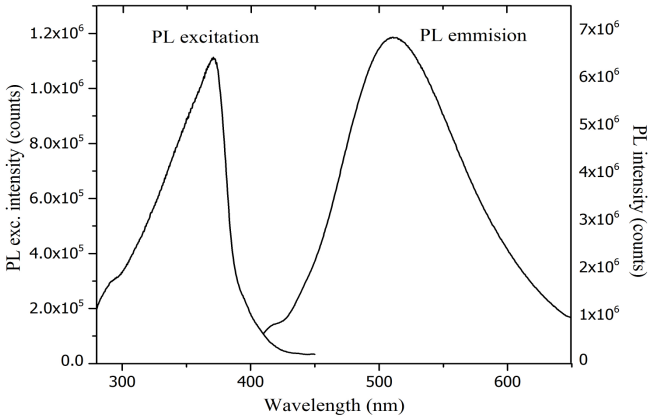

Figure 4. Photoluminescent excitation (PLE) spectrum and photoluminescence spectrum (PL) of Zno nanoparticles.

Application for optical 2-barcode system

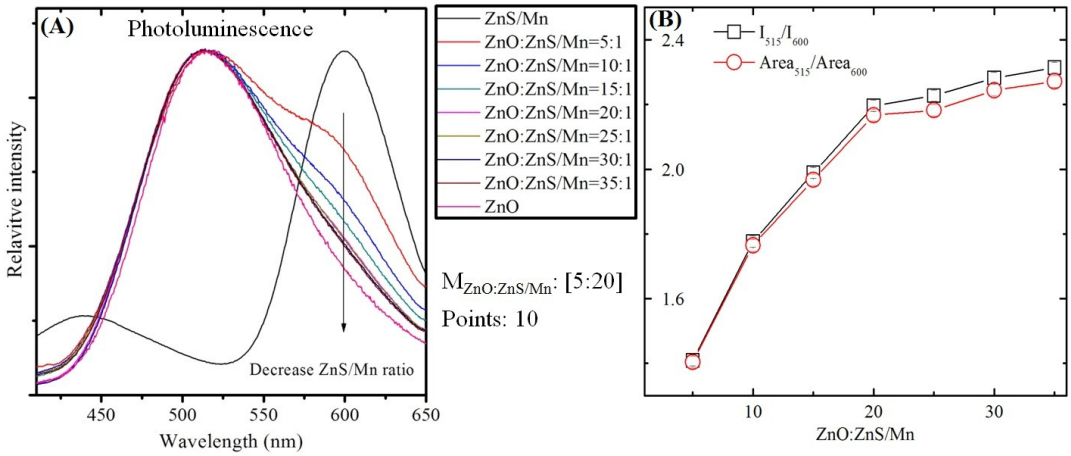

Figure 5. Photoluminescences of the ZnO:ZnS/Mn pellets of different mass ratios (A) and the graph of relative PL intensity (B – square points), intergral intensity ratio (B – circle points) of peaks at 515 of ZnO and 600 nm of ZnS/Mn vs the mass ratio.

Fig. 5A shows the PL observation of the ZnO: ZnS/Mn pellets and the dependence of relative intensity of peak at 515 nm to 600 nm on the mass ratio (Fig. 5B). Decreasing of the proportion of ZnS/Mn results in the decreasing of the relative intensity of the peak at around 600 nm, which was attributed to PL peak of ZnS/Mn. The change of the relative intensity of the peak 600 nm is evaluated by two methods. On one hand, the ratio of the absolute PL intensity of peak at 515 nm to that of peak at 600 nm is taken. The value is labeled as I_{515}/I_{600} and exhibited by a graph in figure 5. On the other hand, the ratio of the total PL intensities of two intervalums at [500 nm – 530 nm] and at [585 nm – 615 nm] is calculated. This value is labeled as $Area_{515}/Area_{600}$ and also shown in figure 5 for several different mass ratios. These two graphs have similar shapes. In application of encryption, it is usually convenient to use the second method. Only two filters, which let the visible light go through at two intervalums around 515 nm and 600 nm are needed. The out come lights could be collected and detected by a simple detector. The ratio of the intensities of the two signals could be calculated by a very simple program, which gives back information about the mass ration of the two semiconductor components. The sizes of the nanoparticles are homogenously small enough to apply in printing or other technique, and hence the products have potential aplicability for encoding purpose.

Conclusion

Mn-doped ZnS (ZnS/Mn) nanoparticles synthesized by sono-chemical co-precipitation are combined with ZnO nanoparticles synthesized by sol-gel method for application in two-barcode encryption. The size of the ZnS/Mn nanoparticles is about 2 nm and of the ZnO nanoparticles is about 50 nm. The PL peak at around 515 nm corresponds to the oxygen vacancy of ZnO material, while that peak at 595 nm corresponds to $^4T_1 - {}^4A_1$ energy transfer of Mn^{2+} in ZnS/Mn materials. The mass ratio change results in the variation of relative PL intensities observed at these two wavelength reigons, which is very promising for manufacturing two-barcode information storage systems for civil security applications.

Acknowledgement

This work is financially supported by Vietnam Nationanl University, Hanoi under the Project number CA.14.11A.

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