Luminescence Properties of ZnS Nanoparticles and Porous Nanospheres Synthesized via Co-Precipitation and Hydrothermal Route

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ZnS nanoparticles were synthesized by hydrothermal and co-precipitation methods. The starting precursors were sodium thiosulfate and zinc chloride for the hydrothermal method; zinc acetate dihydrate and sodium polyphosphate for the co-precipitation method. Scanning electron microscopy (SEM) images of ZnS powder prepared by hydrothermal route show the co-existence of individual ZnS nanoparticles and microspheres formed by the nanoparticles. When acrylamide was added to the process, ZnS porous nanospheres were obtained. Structural properties of ZnS powder prepared by both methods were studied by means of X-ray diffraction (XRD) which revealed that ZnS nanoparticles has the cubic phase and the average size of ZnS nanocrystallites is in the range of 10 nm. Photoluminescence excitation (PLE) and photoluminescence (PL) spectra of ZnS powder synthesized by hydrothermal method indicated that the luminescence intensity of the ZnS nanoparticles was affected by reaction time and surfactant meanwhile a blueshift of about 8 nm compared to bulk ZnS was observed in PLE data of ZnS powder prepared by co-precipitation method, that indicates the quantum confinement effects.

Keywords: Scanning Tunneling Microscopy; Pb; Si(111)

I. INTRODUCTION

ZnS, a wide bandgap semiconductor, is a well-known luminescence material having prominent application in infrared (IR) optical windows [1], flat panel displays [2], sensors and lasers [3, 4]. Recently, there has been increased interest in ZnS based nanostructures with specific shapes due to the hope of new properties. The growth and optical properties of ZnS nanorods [5, 6], nanowires [7–11], nanobelts [12] nanotwin belts [13], nanoballs [14], nanospheres [15–17] have been reported. Some methods for the preparation of ZnS nanocrystallites have been reported recently such as the sonochemical method [18], microwave irradiation [19], sol-gel technique [20], solvothermal method [21], template method [22] etc. Herein, we report the fabrication of ZnS microspheres, porous nanospheres and solid nanospheres by two different preparation techniques: co-precipitation and hydrothermal route. Structural properties of ZnS powder were investigated by X-ray diffraction technique, field-emission electron microscopy and transmission electron microscopy. We have also studied optical properties of ZnS powder prepared by both methods by means of photoluminescence excitation and photoluminescence.

II. EXPERIMENT

All chemicals used were of analytical grade.

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FIG. 1: XRD pattern of the ZnS nanocrystals synthesized by the hydrothermal method, at 200 °C for 4, 7 hours and 4 hours with added acrylamide acting as the surfactant; by co-precipitation method.
A. Synthesis of ZnS microspheres by hydrothermal method

In this experimental procedure, 4.08 g anhydrous ZnCl$_2$, 7.44 g Na$_2$S$_2$O$_3$·5H$_2$O were entered into a 150 ml Teflon-lined stainless-steel autoclave, which was filled with de-ionized (DI) water up to 80% of the total volume. The autoclave was sealed and the interior temperature was maintained at 200°C for 4 and 7 hours. After the reaction was completed, the resulting turbid white liquid was centrifuged, filtered off, washed twice with DI water and absolute ethanol, then finally dried in vacuum (10$^{-2}$-10$^{-3}$ Torr) at 70°C for 15 hours.

B. Synthesis of ZnS porous nanospheres by hydrothermal method

As for the synthesis of porous nanospheres, 3.6 g acrylamide was used as the surfactant in above experiment in same condition.

C. Synthesis of ZnS nanocrystals by co-precipitation method

The starting precursors of the co-precipitation synthesis were zinc acetate dihydrate - Zn(CH$_3$COO)$_2$·2H$_2$O and sodium polyphosphate (PP) - Na(PO$_3$)$_n$ for the co-precipitation process. 40 ml of 1M Zn(CH$_3$COO)$_2$·2H$_2$O was added to an aqueous solution of 40.8 g Na(PO$_3$)$_n$ (Aldrich, 96%, $n \approx 10$). The total volume after the addition was 360 ml. After about 30 min of stirring, 40 ml of a 1M Na$_2$S·9H$_2$O solution is injected into the solution. This mixture was stirred for about 12 hours and we obtained a turbid white fluid. Then the particles were centrifuged (18000 rpm), rinsed with distilled water several times and with ethanol 3 times. At the final step, the particles were dried in vacuum of 10$^{-2}$-10$^{-3}$ Torr.

D. Characterization

The structural properties of obtained samples was examined by X-ray diffraction (XRD) using D8 - Advance - Bruker-Germany equipped with graphite-monochromatized Cu Kα radiation ($\lambda = 1.54056$ Å) at the Faculty of Chemistry, Hanoi University of Science, National University Hanoi. To investigate the morphology, field emission scanning electron microscopy (Hitachi-S-4800, 15 kV - Japan) and transmission electron microscopy (TEM) were utilized. The optical properties of the material were studied by the fluorescent system FL3-22 (JOBIN YVON SPEX FL-3-22 fluorescence spectrophotometer) at the Faculty of Physics, Hanoi University of Science, National University Hanoi. All optical spectra were recorded at room temperature.

III. RESULTS AND DISCUSSION

A. Structural properties

Figure 1 shows the typical XRD patterns of as-prepared ZnS microspheres, porous nanospheres prepared by hydrothermal method and ZnS nanocrystallines synthesized by co-precipitation method. We can see clearly in each of these patterns 3 reflections from (111), (220) and (311) planes, indicating the zinc blende structure (cubic, $\beta$-ZnS). We also observed the typical broadening of the three diffraction peaks, implying that the size of ZnS particles was very small.

Estimating from the Debye-Sherrer formula, the average size of the ZnS nanoparticles prepared by co-precipitation method was about 4 nm. Meanwhile, the av-

| Samples   | 1       | 2       | 3       |
|-----------|---------|---------|---------|
| Temperatures (°C) | 200     | 200     | 200     |
| Reaction time (hours) | 4       | 7       | 4       |
| Added acrylamide | without | without | with    |
| FWHM (radians) | 0.0164  | 0.0118  | 0.0397  |
| $\theta$ (degree) | 14.335  | 14.318  | 14.347  |
| Nanoparticle size (nm) | 9       | 12      | 4       |
average size of ZnS nanoparticles synthesized by hydrothermal method in different conditions was shown in Table I. For this technique, with increase in the reaction time from 4 to 7 hours, a slight increase in size of ZnS nanocrystals prepared without added acrylamide was noted. When acrylamide was added into the reaction and acted as the surfactant, the average size of ZnS nanocrystals decreased significantly to about 4 nm. The surfactant could help reduce the agglomeration of ZnS particles, therefore reduce the average size of ZnS nanocrystals found in the final product.

Figure 2(a) shows a typical FE-SEM image of ZnS microspheres in the samples prepared without using acrylamide. A closer view of the surface region of a ZnS microsphere is shown in Fig. 2(b). We can see clearly that this surface is relatively rough, implying that the shell of microspheres could consist of ZnS nanocrystals. The size of these nanocrystals is about 15 nm, which is in the same order of magnitude with that calculated by Debye-Sherrer’s formula. It is worth noting that in Fig. 2(a), many ZnS aggregates having different forms were observed beside the microsphere structure. A higher resolution FE-SEM image of these aggregates is presented in Fig. 2(c). It is clear that these structures were also formed by ZnS nanocrystals.

Figure 3(a) is the FE-SEM images of ZnS porous nanospheres prepared by using acrylamide as the surfactant. The as-obtained nanospheres display rough surface and the diameter ranges from ~100 nm to 250 nm. Figure 3(b) shows a typical broken nanospheres, indicating the porous structure of the sample. This structural feature can be explained by the generation of SO$_2$ gas bubbles during the synthesizing reaction. In fact, the reaction forming ZnS includes steps as shown in the following equation [17]:

$$(S_2O_3)^{2-} + 2H^+ \rightarrow S + SO_2 + H_2O \quad (1)$$

$$(3S + 2H_2O \rightarrow 2H_2S + SO_2) \quad (2)$$

$$Zn^{2+} + H_2S \rightarrow ZnS \downarrow + 2H^+ \quad (3)$$

Firstly, (S$_2$O$_3$)$^{2-}$ is unstable in acidic solution of Zn$^{2+}$ salt and will transform to form S and SO$_2$, then the element S reacts with H$_2$O to the formation of H$_2$S and SO$_2$ under hydrothermal condition. Finally, Zn$^{2+}$ and H$_2$S combine to make the ZnS. ZnS nanocrystals might aggregate around the gas-liquid interface between SO$_2$ and water, thus the ZnS porous nanospheres might be formed.

Size and morphology of ZnS nanoparticles synthesized by co-precipitation method were investigated by means of TEM. Figure 4 shows a typical TEM image of these particles. We notice that the nanoparticles have relatively round shape and their size varies from few nanometers to few ten nanometers.

**B. Luminescence properties**

In Fig. 5, we report two typical photoluminescence excitation (PLE) spectra of ZnS microspheres hydrothermally synthesized at 200°C for 4 and 7 hours. For both samples, a broad excitation band from 250 to 450 nm was observed with a monitoring wavelength of 440 nm. Within this broad band, two main peaks located at 280 and 360 nm were recognized (Fig. 5), respectively. Compared with that of bulk ZnS (344 nm) [23], the peak at 280 nm ex-
Exhibiting a great blue shift (~64 nm) is interpreted [24] as being due to an increase in the value of s-p electron band gap in the ZnS nanocrystals from quantum confinement. We can therefore attribute this peak to PLE signal stemming from ZnS nanocrystals. The other excitonic transition is surprisingly located at 360 nm, which is longer in wavelength than that of bulk ZnS at 344 nm [23]. The origin of this peak is unclear and under investigation.

Figure 6 shows the PLE spectrum of the ZnS porous nanospheres hydrothermally synthesized with added acrylamide acting as the surfactant. With a monitoring wavelength of 440 nm, a broad excitation band spreading from 250 nm to 350 nm is observed. This band exhibits two main peaks at 280 nm and 320 nm. As mentioned above, the 280 nm PL peak is related to the quantum confinement effect due to the small size of ZnS solid nanospheres. The PLE peak located at 320 nm (3.87 eV) coincides well with A-free exciton transition energy in cubic ZnS [25].

Figure 7 displays the PL spectra of ZnS powder recorded when the samples were photoexcited at 360 nm. The PL spectra of ZnS samples containing microspheres exhibit a broad band having a peak at ~465 nm (Figs. 7(a) and (b)). Meanwhile, a narrower band of higher intensity is observed in the PL spectrum of ZnS samples containing porous nanospheres (Fig. 7(c)). For undoped ZnS nanocrystals, the emission band centered at ~400-470 nm are often assigned to intrinsic defects, i.e. sulfur vacancy, interstitial zinc ... and surface states which strongly depend on the sample synthesis conditions [26].

The optical properties of ZnS prepared by co-precipitation method were presented in Fig. 8. PLE data of ZnS nanoparticles exhibit a blueshift of about 8 nm compared to ZnS bulk, which indicates the quantum confinement effects.

IV. CONCLUSION

In summary, we present the synthesis of ZnS nanoparticles via hydrothermal and co-precipitation route. In the hydrothermal process, ZnS microspheres were formed by the agglomeration of ZnS nanocrystals. ZnS porous nanospheres were also obtained by adding acrylamide into...
the reaction. Due to quantum confinement effect, the photoluminescence properties of ZnS samples containing porous nanospheres exhibited a blue shift (≈64 nm) compared with the PLE peak of bulk ZnS. The hydrothermal route presented in this paper could be used in the fabrication of other inorganic porous and hollow nanospheres. The photoluminescence excitation (PLE) data for ZnS nanocrystals synthesized by co-precipitation method exhibit a blueshift of about 8 nm compared to bulk ZnS, indicating the quantum confinement effects.

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[1] P. Calandra, M. Goffredi, and V. T. Liveri, Colloids Surf. A 160, 9 (1999).
[2] M. Bredol and J. Merikhi, J. Mater. Sci. 33, 471 (1998).
[3] T. Yamamoto, S. Kishimoto, and S. Iida, Physica B 308-310, 916 (2001).
[4] T. V. Prevenslik, J. Lumin. 87-89, 1210 (2000).
[5] H. Wang, Z. Chen, Q. Cheng, and L. Yuan, J. Alloys and Compounds 478, 872 (2009).
[6] W. Yu, P. Fang, and S. Wang, Appl. Surf. Sci. 255, 5709 (2009).
[7] Y. Wang, L. Zhang, C. Liang, G. Wang, and X. Peng, Chem. Phys. Lett. 357, 314 (2002).
[8] M. Lin, T. Sudhiranjan, C. Boothroyd, and K. P. Loh, Chem. Phys. Lett. 400, 175 (2004).
[9] B. Lassen, and P. C. Eklund, Nano Lett. 4, 1663 (2004).
[10] S. Kar, S. Biswas, and S. Chaudhuri, Nanotechnology 16, 737 (2005).
[11] H.-S. Chung, Y. Jung, T. J. Zimmerman, S.-H. Lee, J. W. Kim, S. H. Lee, S. C. Kim, K. H. Oh, and R. Agarwal, Nano Lett. 8, 1328 (2008).
[12] J. Hu, G. Wang, C. Guo, D. Li, L. Zhang, and J. Zhao, J. Lumin. 122-123, 172 (2007).
[13] Y. Li, L. You, R. Duan, P. Shi, and G. Qin, Solid State Commun. 129, 233 (2004).
[14] Y. Zhao, J.-M. Hong, and J.-J. Zhu, J. Cryst. Growth 270, 438 (2004).
[15] X. Yu, L. Yang, S. Yang, and P. Zhou, J. Mater. Res. 22, 1207 (2007).
[16] Q.-Z. Yao, G. Jin, and G.-T. Zhou, Mater. Chem. Phys. 109, 164 (2008).
[17] C. Jiang, W. Zhang, G. Zou, W. Yu, and Y. Qian, Mater. Chem. Phys. 103, 24 (2007).
[18] X. H. Liao, J. J. Zhu, and H. Y. Chen, Mater. Sci. Eng. B 85, 85 (2001).
[19] J. J. Zhu, M. Zhou, J. Xu, and X. Liao, Mater. Lett. 47, 25 (2001).
[20] N. I. Kovtyukhova, E. V. Buzaneva, C. C. Waraksa, and T. E. Mallouk, Mater. Sci. Eng. B 69/70, 411 (2000).
[21] Q. Zhao, L. Hou, and R. Huang, Inorg. Chem. Commun. 6, 971 (2003).
[22] D. Zhang, L. Qi, H. Cheng, and J. Ma, J. Colloid. Interf. Sci. 246, 413 (2002).
[23] J. Li, Y. Xu, D. Wu, and Y. Sun, Solid State Commun. 130, 619 (2004).
[24] L. Brus, IEEE J. Quantum Electron. QE-22, 1909 (1986).
[25] O. Madelung, M. Schultz, and H. Weiss (Eds.), Physics of II-VI and I-VII Compounds, Semimagnetic Semiconductors, in: Landolt-Boernstein, New Series, Group III, vol. 17, Springer, Berlin, (1982), Pt. B.
[26] H.-Y. Lu, S.-Y. Chu, and S.-S. Tan, J. Cryst. Growth 269, 385 (2004).