International Journal of Electrospun Nanofibers and Applications,
Vol.1 No. 2 (July-December, 2015)
ISSN : 0973-628X

Structural Characterization and Photoluminescent Properties of ZnS Nanoparticles Well-dispersed in PVA Nanofibers

Zhengfa Zhou[a, b*], Dian He[b], Weibing Xu[b] Fengmei Ren[b] & Yitai Qian[a]

[a]Department of Chemistry, University of Science and Technology of China, Hefei, 230026, China
[b]Department of Polymer Science and Engineering, Hefei University of Technology, Hefei, 230009, China

Abstract: *Well-dispersed zinc sulfide (ZnS) nanoparticles embedded in poly (vinyl alcohol) (PVA) nanofibers have been successfully prepared by electrospinning technique. The formation of zinc sulfide/poly (vinyl alcohol) nanocomposites was carried out by reacting thiourea with zinc acetate/poly (vinyl alcohol) nanofibers, which were electrospun from the mixture aqueous solution of zinc acetate and poly (vinyl alcohol). Scanning electron microscopy (SEM), transmission electron microscopy (TEM), and selected area electron diffraction (SAED) analyses reveal that zinc sulfide nanoparticles with cubic structure separate from each other with a diameter of about 2 to 3 nm. The photoluminescence spectrum of zinc sulfide/poly (vinyl alcohol) nanocomposites has a 20 nm blue shift compared with that of bulk ZnS sample. Further more, this novel method is easy to operate and involves no toxicant, initiator, surfactant or higher temperature.*

Keywords: *Nanocomposites; ZnS; Poly(vinyl alcohol); Photoluminescence*

1. INTRODUCTION

Semiconductor nanocrystals, especially II–VI quantum dots (such as ZnS and CdS) and their related nanocomposites, have attracted considerable attention due to their unique size quantization effects and potential applications in optoelectronics, optical sensing, biolabeling and biomedicine. [1-5] Thus, varieties of methods have been devoted to fabricating semiconductor nanoparticles, including solvothermal method, electrochemical route, self-assembly process, ion-beam-implantation technique and soft solution reaction, etc. [6-10] Among these approaches, fabrication of nanoparticles with symmetrical structures or a low aggregation is still a big challenge. To solve this problem, supporting matrices including polymer, glass, ceramic and paraffin are used to improve the stability of nanocrystals and reduce the surface defects. [11-13] But most processes require rigorous reaction conditions, using of toxicants (organometallic precursors or H_2S) and complicated operating process.

Electrospinning is a versatile and effective method to generate fibers with a diameter of several tens to hundreds nanometer from a variety of materials [14]. The formed fibers can be applied in membrane technology, tissue engineering, gas sensors, biological reagents, and inorganic nanowires fabrication [15-19]. Wang et al have made a great deal of research to fabricate various inorganic nanoparticles in polymer matrix by

* corresponding author: E-mail: *zhengfazhou@sohu.com*

electrospinning technique. Among these processes, the utilization of H_2S is unavoidable. [11, 20-22].

In this paper, we report our current progress on the extension of the electrospinning technique to prepare well-dispersed ZnS nanoparticles in PVA- nanofibers matrices. This process which is described as Scheme1 involved three steps: (1) Preparing of a sol with suitable zinc acetate ($Zn(Ac)_2$) and PVA content for electrospinning. (2) Spinning of the solution to obtain fibers of $Zn(Ac)_2$/PVA composite. (3) Introducing the sulfur sources to form ZnS nanocrystals in PVA nanofibers. The results reveal that ZnS nanoparticles are equably dispersed in the smooth high aspect ratio polymer nanofibers with a diameter ranging from 2 to 3 nm and no stacking faults. Further more, the whole process is easy to operate and involves no toxicant, initiator, surfactant or higher temperature.

2. EXPERIMENTAL

Poly (vinyl alcohol) (PVA) with an average degree of polymerization of 1700 and a degree of hydrolysis of 99% was obtained from Wanwei Advanced Material Co. Ltd. The other chemicals were purchased from Shanghai Chemicals and used without further purification.

First, 10.0 g aqueous PVA solution (12 wt%) was mixed with zinc acetate solution (4.5 mL, 10 wt%) and acetic acid (1 mL) in a conical flask, followed by vigorous stirring in a water bath at 60 °C for 5 h. Thus, a viscous gel of PVA and zinc acetate mixture was obtained. Then, in a typical electrospinning process, the solution was electrospun at 20 kV positive voltage, 20 cm working distance (the distance between the needle tip and the grounded metal plate), and 1 mL/h flow rate at room temperature; the dense nonwoven mat of nanofibers was collected on the target. Subsequently, the mat was immersed in 0.01 mol/L thiourea ($(NH_2)_2CS$) ethanol solution and the pH of the solution was adjusted to 10. The mat would be gradually changing from white to primrose yellow in several hours. Aftermost, the mat was washed with ethanol for three times and the last product was obtained.

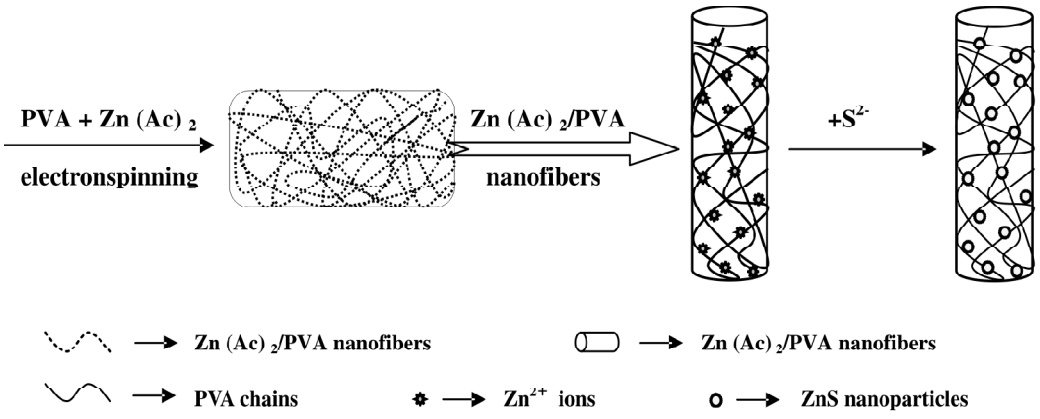
The image of the ZnS/PVA composite nanofibers was observed by field-emission scanning electron microscopy (SEM, JSM-820) and transmission electron microscopy (TEM, H-800; HRTEM, JEOL-2010). The composition of the products was characterized by X-ray photoemission spectroscopy (XPS, ESCALAB-MK-a!) and Fourier-transform infrared spectroscopy (FTIR¡¡spectrum-100). The photoluminescence results were obtained with a UV-365 spectrophotometer.

3. RESULTS AND DISCUSSION

Fig. 1 (a) shows a representative SEM image of $Zn(Ac)_2$/PVA nanofibers produced by electrospinning. The products consist of a large quantity of random deposited fibers and the individual fiber has high aspect ratios. According to the measurements, the average diameter and length of $Zn(Ac)_2$/PVA nanofibers is about 300nm and several millimeters, respectively. In this process, PVA was not only used as a supporting matrix, but also an organizer with hydroxy group which could interact with the zinc ions. And it would

passivate the surface activity of ZnS nanoparticles and avoid aggregation after the sulfur ions were introduced.

To test the existence of zinc ions in the PVA fibers, XPS is used to determine their surface composition. The $Zn2p_{3/2}$ peak is observed at 1022.3 eV from Fig. 2. This corresponds well to the expected values for Zn bounding to oxygen, which also indicates the existence of zinc ions in the polymer fibers. This result can be proven by Fourier-transform infrared spectroscopy. In Fig. 3 (a), a wide strong peak at 3399.9 cm^{-1} is due to the stretch vibration of -OH in pure PVA fibers. The corresponding peak of the $Zn(Ac)_2$/PVA fibers is shift to 3424.4 cm^{-1} as shown in Fig. 3 (b), which means that zinc ions have been coordinated with hydroxy group and the electrophilic inductive effect makes the



Scheme 1: Simplified schematic representation of the formation of ZnS/PVA nanocomposites

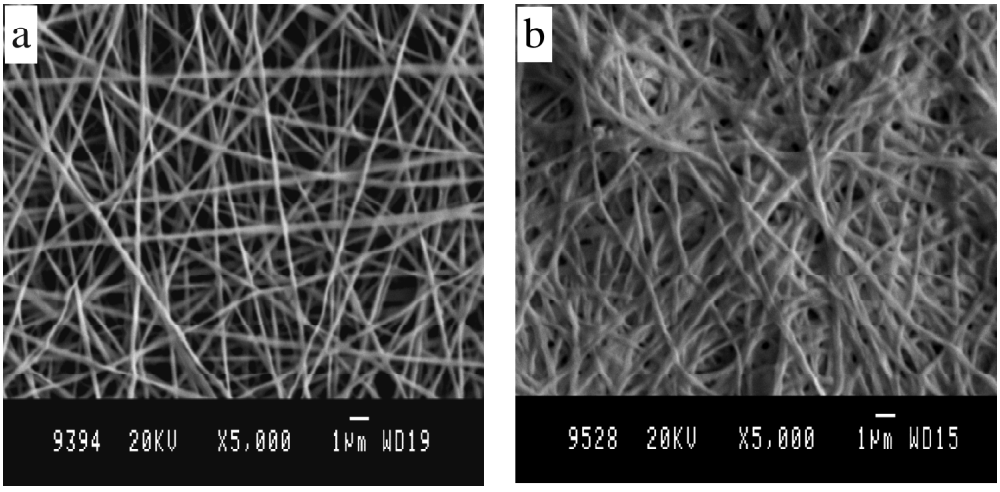


Figure 1: SEM images. (a) $Zn(Ac)_2$/PVA nanofibers prepared by electrospinning; (b) ZnS/PVA nanofibers.

absorption peak of -OH move to a higher vibration frequency. After the sulfur resource was introduced, ZnS nuclei formed and grew into nanoparticles under the drive of combining force between Zn^{2+} ions and S^{2-} ions. The intensity of coordination effect between Zn^{2+} and -OH was decreased and the absorption peak of stretch vibration of -OH in PVA/ZnS fibers (Fig.3 (c)) was located at 3414.8 cm^{-1}, which was lower than that of in $Zn(Ac)_2$/PVA fibers, but still higher than that of in pure PVA fibers. It demonstrated that ZnS coordinated with hydroxy group and polymer matrix might prevent the particles from growing and aggregating further. The color of $Zn(Ac)_2$/PVA fibers is white. After sulfur ions are introduced and nucleation happened, the color of the mat becomes primrose yellow indicating the formation of the ZnS. The image of the ZnS/PVA composite nanofibers (Fig. 1 (b)) is similar to that of $Zn(Ac)_2$/PVA fibers, but the diameter of ZnS/PVA composite nanofibers is bigger than that of $Zn(Ac)_2$/PVA fibers.

TEM is used to observe ZnS nanoparticles in the PVA matrix. The ZnS nanoparticles are embedded and well dispersed in polymer matrix as showed in Fig. 4 (a-b). These ZnS nanoparticles are roughly spherical in shape, separating from each other with a diameter of about 2 to 3 nm. These results are also demonstrated in HRTEM image (Fig. 4 (c)). ZnS nanoparticles are close to spherical and the mean crystal diameter is 3 nm. All these indicate that the polymer matrix could effectively prevent the particles from growing and aggregating further, which is in agreement with those reported by Wang. [20].

The selected area electron diffraction (SAED) patterns (Fig. 4 (d)) clearly show the diffraction rings of ZnS, which can be characterized as 111, 220 and 311 crystalline planes from inner to outer by calculating the ratio of the corresponding radii. Therefore, it reveals that these microcrystalline structures are composed of cubic ZnS (JCPDS NO. 5-566). The SAED data is shown in table 1.

Table 1
Electronic Diffraction Data of ZnS Nanocrystals in PVA Matrix

N_d	*1*	*2*	*3*
R_i (mm)	6.4	10.5	12.3
$d_{Ei} = L\lambda/R_i$ (nm)	0.3138	0.1912	0.1633
d_{Ti} (nm)	0.3118	0.1915	0.1633
$\{hkl\}_i$	111	220	311

The photoluminescence properties of the as-obtained ZnS/PVA composites are detected by spectrophotometer. The PL spectrum illustrated in Fig. 5 shows a broad blue emission with peak position at 430 nm assigned to the electron–hole recombination from internal vacancies for Zn and S atoms. There is a blue shift of about 20nm of the emission band compared with that of the bulk ZnS [23], which could be explained by the quantum size effects of ZnS nanocrystallites. These room temperature photoluminescence properties indicate that the as-prepared material may have potential applications in light-emission optoelectronic devices.

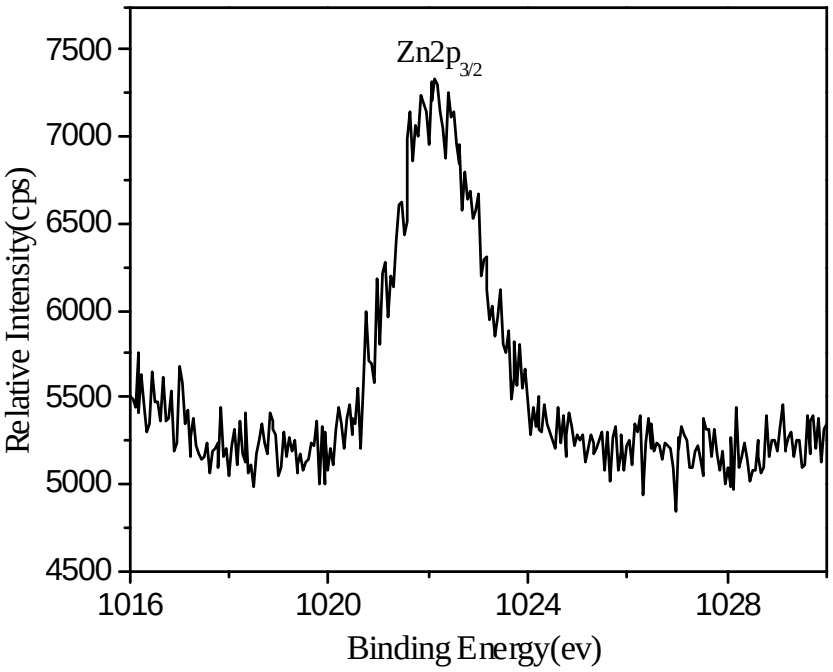


Figure 2: XPS spectrum of $Zn(Ac)_2$/PVA nanofibers prepared by electrospinning

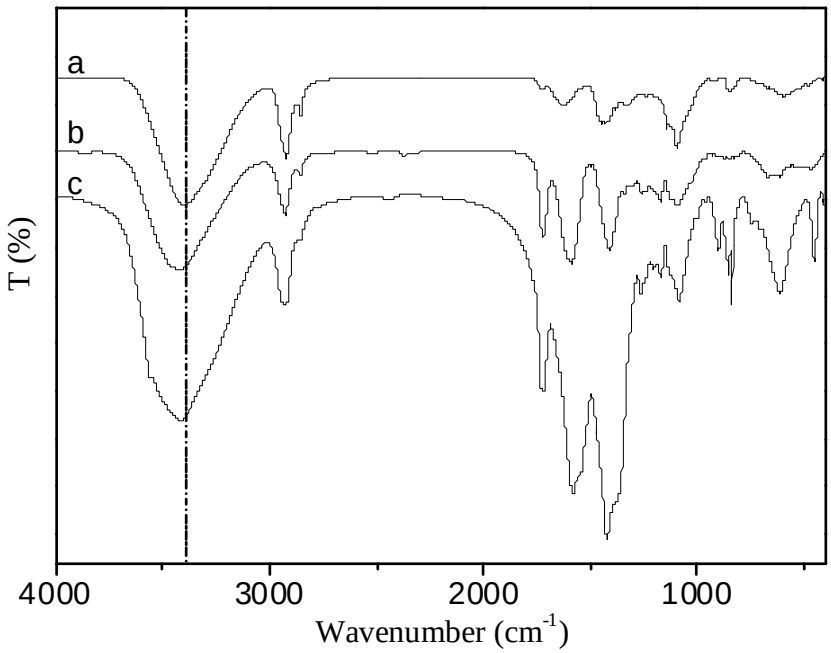


Figure 3: FTIR spectra. (a) pure PVA fibers; (b) $Zn(Ac)_2$/PVA fibers; (c) ZnS/PVA fibers.

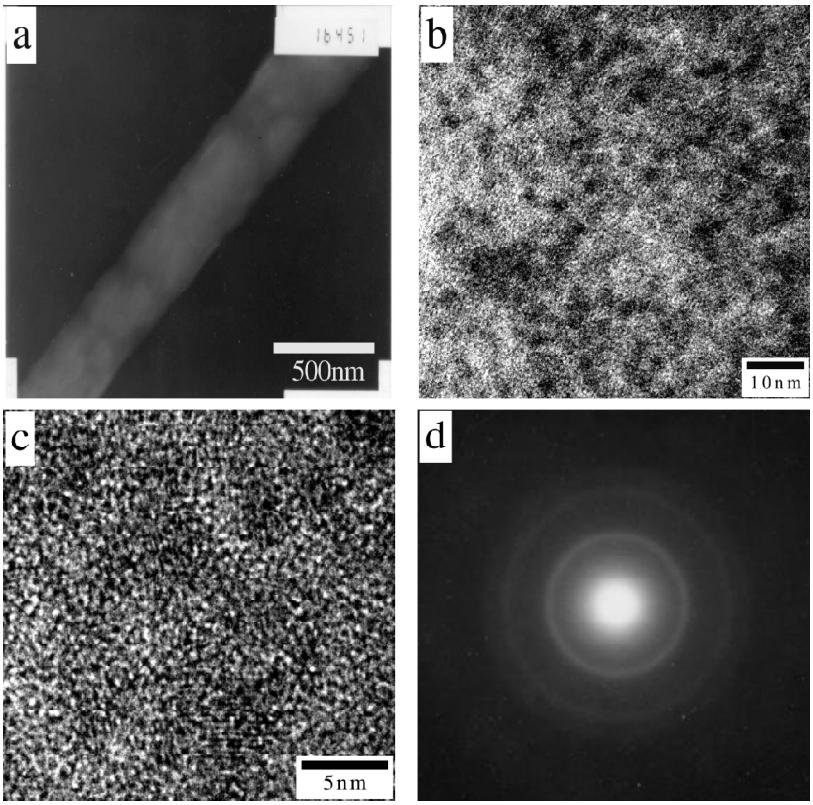


Figure 4: TEM, HRTEM, and SAED images of ZnS nanoparticles formed in PVA nanofibers. (a) TEM; (b-c) HRTM; (d) SAED.

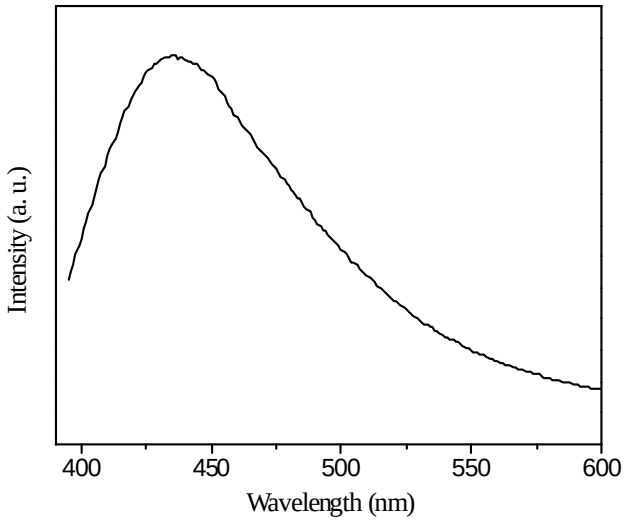


Figure 5: Photoluminescence emission (λ_{ex} =380nm) spectrum of ZnS/PVA nanofibers

4. CONCLUSION

In summary, we present a novel and simple approach to fabricate well-dispersed ZnS nanoparticles with a diameter of 2 to 3 nm in PVA-nanofibers matrix. This as-prepared product integrates the photoelectric, catalytic, etc. properties of ZnS nanoparticles and easily processing capability of PVA nanofibers. This opens a new route to synthesize multifunction nanocomposites.

ACKNOWLEDGEMENTS

The authors would like to acknowledge the academician fund of Hefei University of Technology for its financial support.

References

[1] Z. J. Horva2th, Curr. Appl. Phys. 6 (2006) 145.

[2] J. M. Costa-Ferna´ndez, R. Pereiro, A.S. Medel, Trends Analy. Chem. 25 (2006) 207.

[3] F. Pinaud, X. Michalet, L. A. Bentolila, J. M. Tsay, S. Doose, J. J. Li, G. Iyer, S. Weiss, Biomaterials 27 (2006) 1679.

[4] W. W. Yu, E. Chang, R. Drezek, V. L. Colvin, Biochem. Bioph. Res. Co. 348 (2006) 781.

[5] C. Srinivasan, J. Lee, F. Papadimitrakopoulos, L.K. Silbart, M.H. Zhao, D.J. Burgess, Molecular Therapy 14 (2006) 192.

[6] X. Z. Liu, J. H. Cui, L. P. Zhang, W. C. Yu, F. Guo, Y. T. Qian, Mater. Lett. 60 (2006) 2465.

[7] X. F. Han, R. Liu, Z. D. Xu, W. X. Chen, Y. F. Zheng, Electrochem. Commun. 7 (2005) 1195.

[8] L. L. Wu, Y. S. Wu, Y. Z. Lu, Mater. Res. Bull. 41 (2006) 128.

[9] P. Huber, H. Karl, J. K. N. Lindner, B. Stritzker, Nucl. Instrum. Meth. B. 242 (2006) 170.

[10] R. He, H. C. Gu, Colloid. Surface. A. 272 (2006) 111.

[11] X. F. Lu, Y. Y. Zhao, C. Wang, Adv. Mater. 17 (2005) 2485.

[12] I. O. Mazali, R. Romano, O. L. Alves, Thin Solid Films 495 (2006) 64.

[13] G. G. Yordanov, E. Adachi, C. D. Dushkin, Colloid. Surface. A. 289 (2006) 118.

[14] Z. M. Huang, Y. Z. Zhang, M. Kotaki, S. Ramakrishna, Compos. Sci. Technol. 63 (2003) 2223.

[15] R. Gopal, S. Kaur , Z. W. Ma, C. Chan, S. Ramakrishna, T. Matsuura. J. Membrane Sci. 281 (2006) 581.

[16] Y. Z. Wang, D. J. Blasiolia, H. J. Kimb, H. S. Kimc, D. L. Kaplana, Biomaterials 27 (2006) 4434.

[17] R. Luoh, H. T. Hahn, Compos. Sci. Technol. 66 (2006) 2436.

[18] M. Ignatova, K. Starbova, N. Markova, Carbohyd. Res. 341 (2006) 2098.

[19] A.M. Azad, Mater. Sci. Engineering A. 435 (2006) 468.

[20] H. Y. Wang, X. F. Lu, Y. Y. Zhao, C, Wang, Mater. Lett. 60 (2006) 2480.

[21] X. F. Lu, X. C. Liu, W. J. Zhang, C. Wang, Y. Wei, J. Colloid. Interf. Sci. 298 (2006) 996.

[22] Y. Z. Wang, Q. B. Yang, G. Y. Shan, C. Wang, J. S. Du, S. G. Wang, Y. X. Li, X. S. Chen, X.B. Jing, Y. Wei, Mater. Lett. 59 (2005) 3046.

[23] P. Yang, M.K. Lü, F.Q. Meng, C.F. Song, D. Xu, Opt. Mater. 27 (2004) 103.