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Original Article

Synthesis of ZnO Nanoparticles/Nanofibers and Their Luminescence via Electrospinning

Pham Hung Vuong[1,*], Nguyen Duc Trung Kien[1], Tran Trong An[1], Ta Quoc Tuan[1], Pham Van Huan[1], Nguyen Dac Thong[1,2], Vu Thi Phuong Thuy[1,3], Le Van Toan[1,4]

[1]*Advanced Institute for Science and Technology (AIST), Hanoi University of Science and Technology (HUST), 1 Dai Co Viet, Hanoi, Vietnam*

[2]*School of Engineering Physics, Hanoi University of Science and Technology (HUST), 1 Dai Co Viet, Hanoi, Vietnam*

[3]*Trade Union University, 169 Tay Son, Hanoi, Vietnam*

[4]*Le Quy Don Technical University, 236 Hoang Quoc Viet, Hanoi, Vietnam*

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Abstract: This article reports on the synthesis procedure of ZnO nanoparticles/nanofibers structure by electrospinning method using Zinc acetate and polyvinylpyrrolidone (PVP) surfactant as reagents and evaluates their luminescent properties. The microstructure of ZnO nanoparticles/nanofibers was observed by FE-SEM. The phase formation of ZnO nanoparticles/nanofibers was studied by XRD. ZnO nanoparticles/nanofibers structure shows strong luminescence centering at 660 nm, which has potential applications in solid-state lighting.

Keywords: ZnO, nanofibers, luminescence, electrospinning, nanoparticles

1. Introduction

In recent years, red emission of the phosphors has become a great interest in solid-state lighting [1, 2]. Many phosphors are being developed for potential applications in lighting such as Eu^{2+} doped CaS

*Corresponding author.
Email address: vuong.phamhung@hust.edu.vn

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[3], $CaSrAlSiN_3:Eu^{2+}$ [4], and Eu^{2+}/Mn^{2+} doped $Ca_3(PO_4)_2$ [5]. However, most of the above-mentioned materials need activation materials to induce light emission which is costly for large scale production. ZnO nanomaterials have received considerable attention in solid-state lighting because of its abundance in the earth and simple processing. There are a lot of published documents on reposting the microstructure and luminescence of ZnO nanomaterials [6,7]. Most of them revealed that ZnO nanomaterials displayed both ultraviolet near-band-edge emission (NBE) and visible emission which is limited to their applications in solid-state lighting [8,9]. Therefore, this study is an attempt to synthesize ZnO nanoparticles/nanofibers using electrospinning method for controlling the specific visible emission of ZnO. The microstructures of the ZnO nanoparticles/nanofibers were characterized by field emission scanning electron microscopy (FE-SEM). Light emission of ZnO nanoparticles/nanofibers was determined by photoluminescence spectroscopy.

2. Experimental Procedure

ZnO nanoparticles/nanofibers were synthesized by electrospinning using zinc acetate (99.99 %, Sigma-Aldrich) / polyvinylpyrrolidone (PVP, 99.9 %, Sigma-Aldrich) at room temperature. ZnO nanofibers were synthesized by electrospinning using 20% weight (wt) amount of PVP. After electrospinning process, ZnO nanofibers were pulled out of aluminium foil and placed inside the furnace (Nabertherm, Germany) which was adjusted to the temperature of 600 ^oC at the heating rate of 10 $^oC\ min^{-1}$ for 2 h in the ambient atmosphere. After which, the system cooled to room temperature naturally for the formation of ZnO nanoparticles/nanofibers structures. The crystalline structures of the ZnO nanoparticles/nanofibers were characterized by X-ray diffraction (XRD, D8 Advance, Bruker, Germany). The microstructure was determined by field emission scanning electron microscopy (JEOL, JSM-6700F, JEOL Techniques, Tokyo, Japan). The luminescent properties of ZnO nanoparticles/nanofibers were determined by NANO LOG spectrofluorometer (Horiba, USA) using 450 W Xe arc lamp. For comperative purpose, ZnO nanorods synthesis by hydrothermal method was also included in this study.

3. Results and Discussions

Figure 1 shows the schematic diagram of electrospinning process for ZnO nanoparticles/nanofibers. Zinc acetate was mixed with PVP surfactant to induce specific viscosity solution for electrospinning process. Under the high electrical voltage of 10 KV, the zinc solution was converted into nanofibers and were deposited on the aluminium foil collector. The as-electrospinning ZnO structure displayed nanofiber morphology under a scanning electron microscope (SEM). Upon thermal annealing of 600 ^oC, PVP surfactant was evaporated and the smooth nanofibers were converted into rough morphology fibers thereafter, namely, ZnO nanoparticles/nanofibers.

The microstructures of the ZnO particles/nanofibers synthesized by electrospinning are shown in Figure 2 (A-B). The synthesized ZnO nanostructure shows that a nanofiber with the diameter ~70 nm was constructed from nanoparticles with the diameter of ~ 20 nm as building units (Figure 1A). A high magnification view of ZnO nanostructure displayed the crystal plane with the interfacing of 0.2476 nm which is consistent with the plane of wurtzite structure of ZnO [10]. The electron diffraction (ED) revealed that ZnO displayed nanocrystal materials.

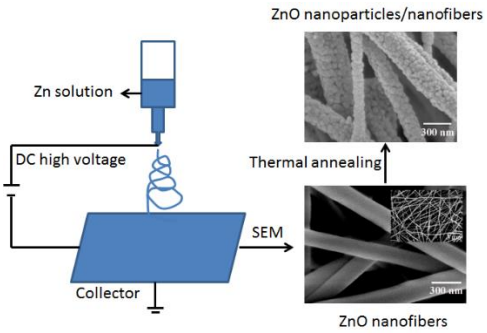

Figure 1. The schematic diagram for electrospinning of ZnO nanoparticles/nanofibers.

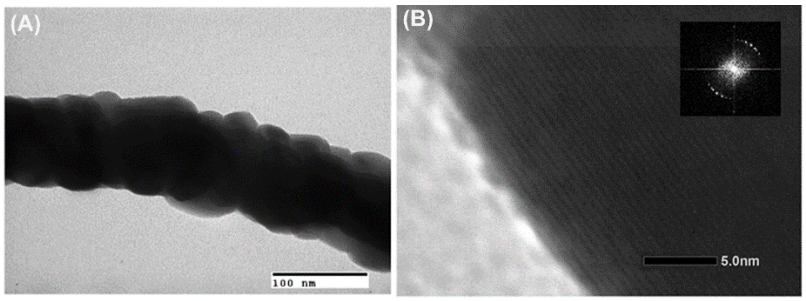

Figure 2. (A)TEM image showing the microstructures of the ZnO nanoparticles/nanofibers.
(B) HR-TEM image showing the highly crystalline structure of ZnO.

Figure 3 shows the typical XRD patterns of the ZnO nanoparticles/nanofibers synthesized by electrospinning. ZnO showed a relatively strong peak at $2\theta = 31.8^o$, 34.4^o, 36.1^o, 47.4^o, 56.50^o, 62.80^o, corresponding to the (100), (002), (101), (102), (110), (103) planes. All of the peaks can be indexed to the crystalline hexagonal wurtzite ZnO (JCPDS 36−1451) without any evidence of impurities, indicating that ZnO nanoparticles/nanofibers have been synthesized successfully. These results indicate that ZnO nanoparticles/nanofibers synthesized by electrospinning displayed a highly crystalline structure consistent with the HR-TEM image (Figure 2B).

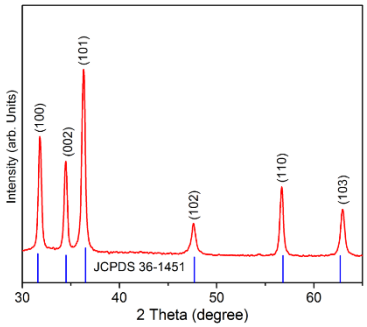

Figure 3. XRD patterns of the ZnO nanoparticles/nanofibers.

Figure 4 shows photoluminescence (PL) spectra of ZnO nanoparticles/nanofibers synthesized by electrospinning in comparison with ZnO nanorods. ZnO nanorods showed a relative strong visible emission peak at ~ 530 nm and one weak near−band−edge (NBE) emission of ~ 380 nm. Unlike the

ZnO nanorods, the visible emission peak of ZnO nanoparticles/nanofibers shifted to a longer wavelength of ~ 660 nm, and NBE peak disappeared. The dominated visible emission peak in the PL in ZnO suggested that oxygen vacancy defects exist in ZnO [11,12]. However, it should be noted that the visible emission peak of ZnO nanoparticles/nanofibers was much higher than that of ZnO nanorods. This significant higher visible emission of ZnO nanoparticles/nanofibers could be explained by the high concentration of ZnO nanoparticles on ZnO nanofiber surface, and therefore a relatively high number of defects at the surface were formed. The defects interfaced with each other to form defect energy bands resulting in the higher visible emission, inset of Figure 4.B.

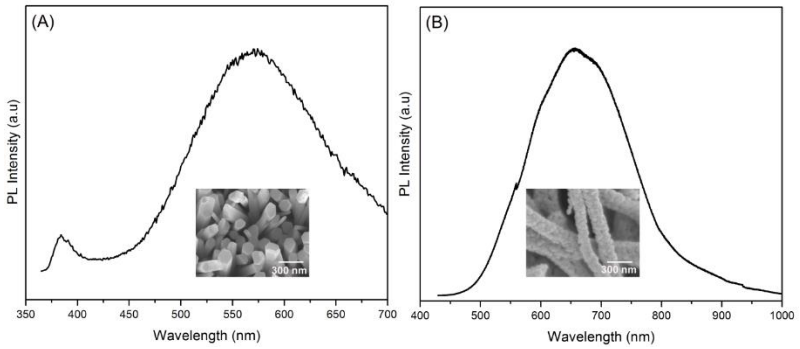

Figure 4. Photoluminescence of ZnO nanorods (A) and ZnO nanoparticles/nanofibers (B).

4. Conclusions

ZnO nanoparticles/nanofibers have been synthesized successfully by electrospinning method. In particular, ZnO nanofibers with the diameter of ~ 70 nm were formed from nanoparticles with the diameter of ~ 20 nm. ZnO nanoparticles/nanofibers showed strong red visible luminescence which has a potential application in solid-state lighting.

Acknowledgments

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