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Short communication

Controlled synthesis of defects-containing ZnO by the French process modified with pulsed injection and its luminescence properties

Busarakam Charnhattakorn [a], Tawatchai Charinpanitkul [a], Akawat Sirisuk [a], Varong Pavarajarn [a,b,*]

[a] Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University, Bangkok 10330, Thailand
[b] National Center of Excellence for Environmental and Hazardous Waste Management, Chulalongkorn University, Bangkok 10330, Thailand

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Abstract

Zinc oxide (ZnO) nanoparticles containing oxygen vacancies were synthesized by the French process modified with pulsed injection of nitrogen. Zinc vapor was generated by evaporation of zinc foil and carried by a carrier gas to react with co-currently supplied air. During the reaction, nitrogen gas was injected in pulse, perpendicular to the flow direction of both zinc vapor and air. Low partial pressure of oxygen and turbulence caused by pulsed injection yielded uniform ZnO nanotetrapods that contained oxygen vacancies. The content of oxygen vacancies depended upon the characteristics of the pulse, i.e. flowing and non-flowing period of the gas, pulsing cycle time, and the supplied pressure of the injected gas. Strong correlation between the presence of oxygen vacancies and the intensity of green emission in the photoluminescence spectra of ZnO was also observed.

Keywords: B. Defects; Zinc oxide; Synthesis; Luminescence; Pulse

1. Introduction

Based on unique properties beneficial to various applications, zinc oxide (ZnO) has attracted considerable attention. Nevertheless, many promising applications of ZnO, e.g. hydrogen storage [1], biosensors [2], and visible-light nanophosphors [3], rely on defects, mainly oxygen vacancies, within the structure of ZnO. Yet most synthesizing techniques for ZnO with controlled defects are either complicated processes, such as chemical vapor deposition [4], or involving with secondary metal doping [5], all of which are impractical for mass production of ZnO.

In the commercially used French process, molten zinc is vaporized and instantly oxidized by air into ZnO powder. Although high-purity ZnO can be produced, high temperature (i.e., 1000–1400 °C) is needed to ensure complete oxidation and to avoid residual Zn metal in the product. Moreover, the process often results in products with mixed morphology because of non-uniform crystallization conditions [6].

In this work, pulsed injection of gas was introduced to the thermal oxidation of zinc vapor. This contribution aims to propose a technique adaptable to mass production of ZnO nanocrystals that can conveniently control defects within their structure.

2. Experimental

This synthesis was based on the reaction between zinc vapor, evaporated from high purity zinc foil (99.99% purity), and dried air. The zinc foil was put into annular section of the double-tube configuration shown in Fig. 1. As the reactor was heated to 800 °C, nitrogen (N_2) gas was supplied through the annulus at 1.25 l/min to carry evaporated zinc vapor to react with air fed at 0.65 l/min in the inner tube. During the reaction, another stream of N_2 was supplied, in pulse, perpendicular to the streams of zinc vapor and air. The duration of flowing and non-flowing (i.e., ‘‘ON’’ and ‘‘OFF’’) periods for the N_2 pulse was varied from 2 s/9 s, 5 s/6 s and 8 s/3 s. The supplied pressure for the N_2 pulse was also varied within the range of 1.5–3 bar. The synthesized ZnO particles were captured via a filter and then characterized by X-ray diffraction (XRD, SIEMENS D5000), scanning electron microscopy (SEM, HITACHI S3400), X-ray

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* Corresponding author. Tel.: +66 2 218 6890; fax: +66 2 218 6877.
E-mail address: Varong.P@chula.ac.th (V. Pavarajarn).

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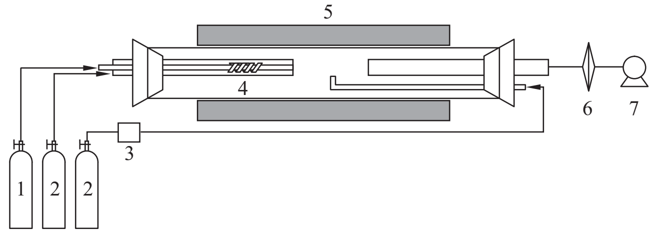

Fig. 1. Schematic diagram of experimental setup: (1) supplied air, (2) supplied nitrogen gas, (3) solenoid valve controlled by timer, (4) zinc foil, (5) electrical furnace, (6) filter and (7) vacuum pump.

photoelectron spectroscopy (XPS, AMICUS ESCA3400 operated using MgKα radiation) and photoluminescence spectroscopy (PL, Perkin Elmer LS55 operated using the excitation at wavelength of 325 nm at room temperature).

3. Results and discussion

3.1. Characteristics of the synthesized ZnO

Based on XRD analysis, all products were found to be ZnO in wurtzite structure without contamination from other crystalline phases (results not shown), confirming the complete oxidation of zinc vapor into ZnO. For the experiment without the N_2 pulse, the product with different morphologies was obtained. Large tetrapods with legs of about 1 μm in length were found mixed with irregular-shaped nanoparticles (Fig. 2a). On the other hand, when the N_2 pulse was introduced to the reaction zone, tetrapod ZnO with nail-like legs was mainly found as shown in Fig. 2b. The legs had diameter in the range of 50–120 nm and flared out to form hexagonal facet at the end. According to the position of N_2 pulsed injection (Fig. 1), ZnO nuclei were already formed before they reached the N_2 injection point. The N_2 pulse perpendicular to the streams of zinc vapor and air could create turbulence to enhance gas mixing that increased formation of ZnO_x vapor. Consequently, deposition of ZnO_x onto the ZnO nuclei increased, resulting in bigger diameter at the end of the tetrapod legs [7]. The enhanced gas mixing aided by the N_2 pulse also resulted in products with uniform morphology.

The O1s XPS spectra of the obtained products could be deconvoluted into three Gaussian peaks. The peaks centered at 533.21 ± 0.3, 531.76 ± 0.15 and 530.11 ± 0.06 eV represent O^{2-} ions in the chemisorbed species (O_H), in the oxygen-deficient region (O_V) and in oxygen lattice of ZnO (O_L), respectively [8]. It has also been reported that the change in the intensity of the signal for O_V is connected in part to the variation

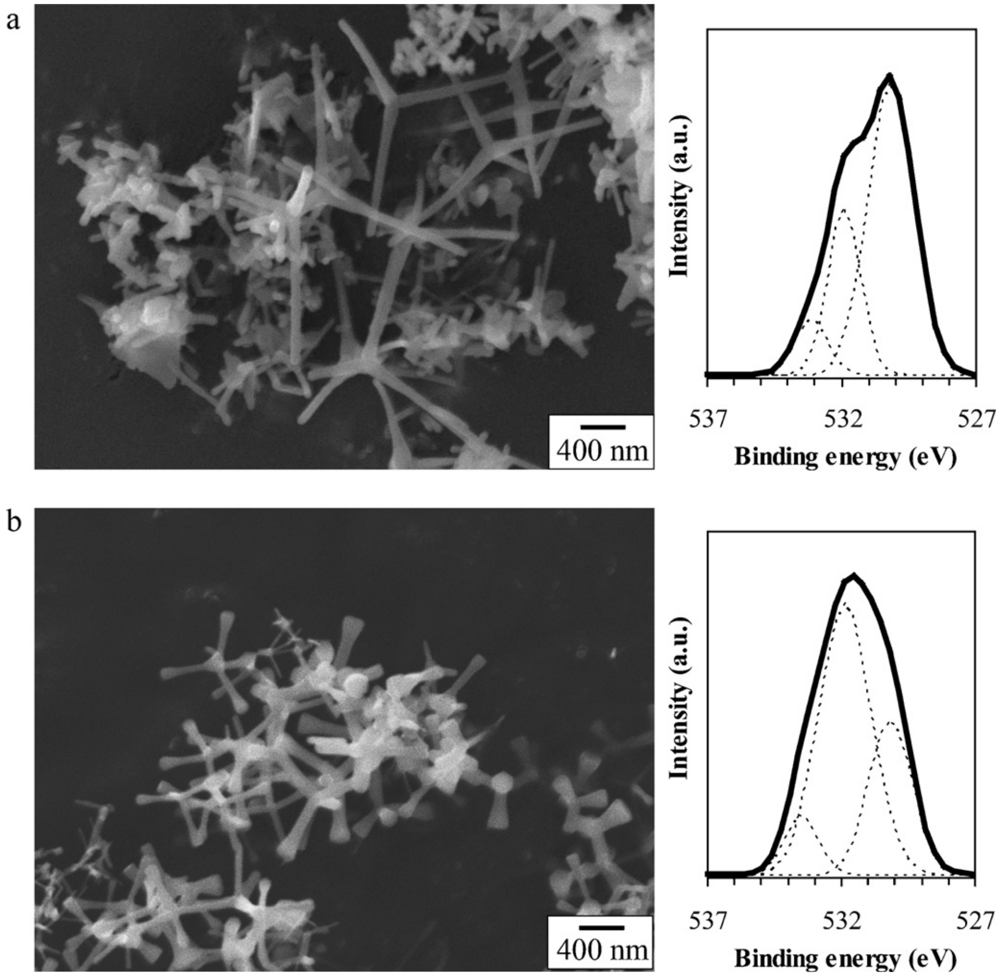

Fig. 2. Micrographs and corresponding O 1s XPS spectra of ZnO synthesized: (a) without N_2 pulsed injection and (b) with 5 s-ON/6 s-OFF N_2 injection cycle.

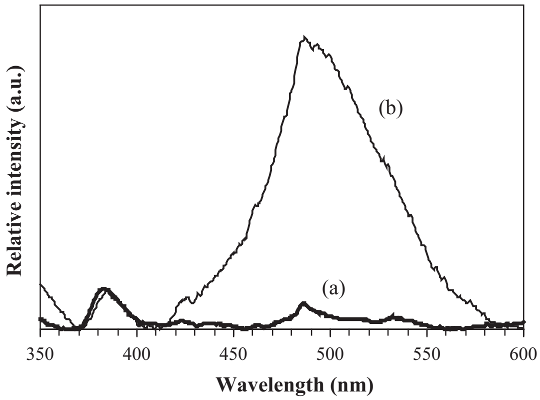

Fig. 3. Photoluminescence spectra of ZnO synthesized: (a) without N_2 pulsed injection and (b) with 5 s-ON/6 s-OFF N_2 injection cycle.

in the concentration of oxygen vacancies in the sample [9]. According to Fig. 2, it was clear that the fraction of oxygen vacancies in ZnO synthesized with the aid of the N_2 pulse was much higher than that in ZnO synthesized without the N_2 injection. It was also found that the intensity of green emission in the PL spectra (at c.a. 490 nm) of the sample was dramatically enhanced (see Fig. 3) by the pulsed injection, while that of ultraviolet (UV) emission at 385 nm was not affected.

3.2. Effect of pulsed injection

The effect of the pulsing characteristics on properties of the product was investigated by varying duration of ON and OFF period for the N_2 pulse cycle. The results were compared with the experiment without any N_2 injection. Based on experimental results, the longer ON period could provide the higher fraction of oxygen vacancies in the synthesized product. The fraction of O_V in the product, calculated from relative peak area of the deconvoluted O_V signal with respect to the total signal for O 1s spectra, increased from 39.0 to 61.9 and 63.8% when the ON period was prolonged from 2 to 5 and 8 s, out of the total cycle time of 11 s, respectively. These values were significantly higher than that from the sample synthesized without N_2 injection (i.e., 29.2%). With the longer pulse injection, prolonged period of oxygen with lower partial pressure within the reaction zone could lower probability of zinc vapor to be fully oxidized and bonded to the surface of the ZnO nuclei previously formed [10]. Notwithstanding, the turbulence caused by the pulsed injection enhanced the mixing between zinc vapor and oxygen and prevented the formation of zinc metal clusters. It should be noted that all samples had roughly the same content of O_H in the range of 8.2–9.8%.

Interestingly, when N_2 was continuously supplied to the reaction zone instead of being pulsed, which should cause the partial pressure of oxygen to be constantly low, the synthesized product contained much lower oxygen vacancies (i.e., O_V of 27.8%) than that synthesized with the N_2 pulse. The result indicated that oxygen partial pressure was not the only factor affecting the formation of defects within the synthesized product. The turbulence caused by pulsed injection would provide a great effect as well. One factor that affected the turbulence caused by the pulsing was the pressure of the supplied N_2. When the N_2 pulse was supplied at significantly higher pressure than that in the reactor, there was a surge in the flow rate of N_2 for very brief period of time (within 0.2 s) at the beginning of the ON period of the pulsing cycle, after which the flow rate returned to the set value. This supplying pressure was found to affect the formation of defects in the ZnO products. With the 5 s-ON/6 s-OFF pulsing, the fraction of O_V decreased from 61.9 to 60.9 and 58.6%, when the N_2 supplying pressure was reduced from 3 to 2 and 1.5 bar, respectively. Nevertheless, the effect of the supplying pressure was not as significant as that of the pulsing characteristics. The product synthesized with the pulsing cycle time of 2 s (1 s-ON/1 s-OFF with the supplying pressure of 3 bar) showed dramatic drop in O_V fraction to only 29.9%.

3.3. Green luminescence of ZnO

In general, ZnO exhibits both UV and visible light emissions in its PL spectra. Out of reports in visible light emission, the origin of green emission is still controversial. Although oxygen vacancies have been mostly attributed as the source of the green emission [11], other kinds of defects such as zinc vacancies [12], oxygen interstitials [13], and antisite oxygen [14] have been claimed as well. The inconsistency may come from the fact that the PL properties of ZnO are affected by its size and morphology [4,11], but it is quite difficult to synthesize ZnO containing different amounts of defects without changing size and morphology. In this work, however, size and morphology of ZnO prepared were fairly uniform, yet the amount of oxygen vacancies could be varied by changing the pulsing conditions. The intensity ratio of green-to-UV emission (I_{green}/I_{UV}) observed was plotted against the fraction of O_V detected from ZnO, to verify the involvement of oxygen vacancies in the green emission. Fig. 4 indicates a strong correlation between the intensity of the green emission and the fraction of oxygen vacancies presenting in ZnO. To the best of our knowledge, this is the first time that such correlation is presented. Nevertheless, it should be noted that the signal for O_V does not completely correspond to the presence of oxygen vacancies [9], which

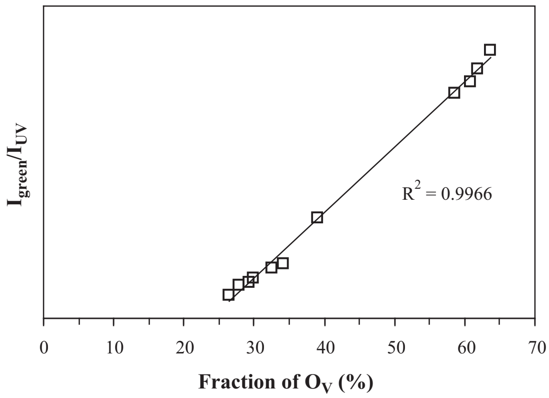

Fig. 4. Correlation between the intensity ratio of green-to-UV emission (I_{green}/I_{UV}) versus the fraction of O_V in ZnO synthesized by various conditions.

explains why our data in Fig. 4 predicts no green emission when the fraction of O_V is lower than 20%.

4. Conclusion

In this work, the introduction of the N_2 pulse to enhance the reaction between zinc vapor and oxygen in the French process was demonstrated as a convenient approach to control oxygen vacancies within ZnO nanocrystals, without forming unreacted zinc metal clusters. The content of oxygen vacancies in the product depends upon the characteristics of the N_2 pulse. The longer N_2 pulse could provide higher mixing beneficial to higher growth of tetrapod ZnO with higher oxygen vacancies. This is the first report on the relationship between oxygen vacancies and the intensity of green emission of tetrapod ZnO with uniform size and morphology.

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References

[1] M. Ahmad, Rafi-ud-Din, C.F. Pan, J. Zhu, Investigation of hydrogen storage capabilities of ZnO-based nanostructures, J. Phys. Chem. C 114 (6) (2010) 2560–2565.

[2] Z. Yang, Z. Ye, B. Zhao, X. Zong, P. Wang, Synthesis of ZnO nanobundles via sol–gel route and application to glucose biosensor, J. Sol–Gel Sci. Technol. 54 (3) (2010) 282–285.

[3] P.K. Sharma, M. Kumar, A.C. Pandey, Green luminescent ZnO:Cu^{2+} nanoparticles for their applications in white-light generation from UV LEDs, J. Nanopart. Res. (2010), doi:10.1007/s11051-010-9916-3.

[4] T.L. Phan, S.C. Yu, R. Vincent, N.H. Dan, W.S. Shi, Photoluminescence properties of various CVD-grown ZnO nanostructures, J. Lumin. 130 (7) (2010) 1142–1146.

[5] L.J. Li, K. Yu, Y. Wang, Z.Q. Zhu, Photoluminescence and field emission properties of Sn-doped ZnO microrods, Appl. Surf. Sci. 256 (11) (2010) 3361–3364.

[6] S. Mahmud, M.J. Abdullah, G.A. Putrus, J. Chong, A.K. Mohamad, Nanostructure of ZnO fabricated via French process and its correlation to electrical properties of semiconducting varistors, Synth. React. Inorg., Met. – Org., Nano-Met. Chem. 36 (2) (2006) 155–159.

[7] Y.N. Zhao, M.S. Cao, H.B. Jin, L. Zhang, C.J. Qiu, Catalyst-free synthesis, growth mechanism and optical properties of multipod ZnO with nanonail-like legs, Scripta Mater. 54 (12) (2006) 2057–2061.

[8] H.H. Wang, C.S. Me, The effects of oxygen partial pressure on the microstructures and photocatalytic property of ZnO nanoparticles, Phys. E 40 (8) (2008) 2724–2729.

[9] M. Chen, X. Wang, Y.H. Yu, Z.L. Pei, X.D. Bai, C. Sun, R.F. Huang, L.S. Wen, X-ray photoelectron spectroscopy and auger electron spectroscopy studies of Al-doped ZnO films, Appl. Surf. Sci. 158 (1–2) (2000) 134–140.

[10] Y.K. Tseng, H.C. Hsu, W.F. Hsieh, K.S. Liu, I.C. Chen, Two-step oxygen injection process for growing ZnO nanorods, J. Mater. Res. 18 (12) (2003) 2837–2844.

[11] L.Y. Zhang, L.W. Yin, C.X. Wang, N. Lun, Y.X. Qi, D. Xiang, Origin of visible photoluminescence of ZnO quantum dots: defect-dependent and size-dependent, J. Phys. Chem. C 114 (21) (2010) 9651–9658.

[12] Y.W. Heo, D.P. Norton, S.J. Pearton, Origin of green luminescence in ZnO thin film grown by molecular-beam epitaxy, J. Appl. Phys. 98 (7) (2005) 073502.

[13] D. Li, Y.H. Leung, A.B. Djurisic, Z.T. Liu, M.H. Xie, S.L. Shi, S.J. Xu, W.K. Chan, Different origins of visible luminescence in ZnO nanostructures fabricated by the chemical and evaporation methods, Appl. Phys. Lett. 85 (9) (2004) 1601–1603.

[14] B.X. Lin, Z.X. Fu, Y.B. Jia, Green luminescent center in undoped zinc oxide films deposited on silicon substrates, Appl. Phys. Lett. 79 (7) (2001) 943–945.