Fabrication of ZnO Hollow Microspheres Organized by ZnO Nanorods via Single-step Hydrothermal Process

Ying-Ying LI*

Public Security Fire Forces College, Kunming 650208, China

waiwailyy@163.com

*Corresponding author

Keywords: ZnO, Nanorods, Hydrothermal, Optical properties.

Abstract. Micrometer scale hollow ZnO dandelions organized by ZnO nanorods were prepared by single-step hydrothermal process. The diameter of the nanorods with the pencil shape tip is estimated to be 150-500nm. The length of the nanorods is more than 2μm. Structure analysis indicated that the as-prepared products were wurtzite structure with high crystallinity. The ZnO nanorods microspheres were found to have excellent UV emission properties at room temperature. These kinds of hollow spherical structures may find potential applications in photocatalysis, light-weight composite fillers, UV nano/micro-optoemission devices and photoanodes of dye-sensitized solar cells.

Introduction

The Kirkendall effect normally refers to comparative diffusive migrations among different atomic species in metals and/or alloys under thermally activated conditions[1]. For example, because of the difference in atomic diffusivities, zinc diffuses into the copper faster than the copper diffuses into the brass in a brass-copper interface[2]. A common result from this process is generation of porosity in the low-melting component side of the diffusion couple. Recently, a process analogous to the Kirkendall effect has been successfully developed for nanoscale fabrication of a variety of hollow crystals, including core-shell metal-metal-oxide structures[3].

As a special class of materials, metal oxide hollow spheres in nano/microscales have attracted great investigative interest due to their unique properties, such as low density, high specific surface area and good permeability, and so on. This kind of structure has wide potential applications in adsorption, catalysis, biomedical diagnosis, delivery of drugs, photonic crystals, acoustic insulation, and light-weight composite fillers[4-7]. The low dimensional, wide band gap (3.37eV) semiconductor-zinc oxide (ZnO) with large exciton binding energy (60meV) at room temperature has been so far applied in many aspects, such as nanoscale lasers[8], piezoelectric devices[9], and sensors[10]. Especially, hollow ZnO spheres with nanowires grown on both inner and outer surfaces of the spherical shells are very beneficial to applications in photocatalytic, acoustic insulation, light-weight composite fillers, and photoanodes of dye-sensitized solar cells owing to their densities and much higher surface to volume ratio as compared to solid spheres and hollow shell structures without nanowires [11].

In this article, micrometer scale hollow ZnO dandelions organized by ZnO nanorods were formed via hydrothermal method, following a modified Kirkendall process. To character the crystal structures of samples, the X-ray diffraction (XRD) were investigated. The surface morphology was studied with a scanning electron microscopy (SEM). The optical properties of the ZnO nanorods arrays were investigated by the photoluminescence (PL) spectrometer and optical absorption spectra. In principle, a lot of metal oxides and metal-semiconductor composites can be obtained in this synthetic architecture. Hopefully, they can be applied in many fields, such as light-generated electrons, three-dimensional lasing, and new photocatalysts.

Experimental

Materials

All chemicals were analytical-grade reagents and were purchased from Shanghai Chemical Reagent Corp. The zinc powder (99.99% purity) was polished, washed by acetone, ethanol and distilled water for several times, and dried in the oven. Tetramethylammoniumhydroxide (TMAOH, 25%) were used as reactants without further purification.

Preparation of Micrometer Scale Hollow ZnO Dandelions Organized by ZnO Nanorods

5mmol of the Zn powder were put into a 50mo Teflon-lined stainless autoclave within 35ml aqueous solution of 0.5M TMAOH. The autoclave was heated to 180 ℃ for 2-24h in the oven. After the reaction, the specimen was completely washed with absolute ethanol and Milli-Q water for several times. The sample was dried in vacuum at 60 ℃ for 12h.

Characterization

The morphologies of the as-synthesized ZnO nanorods arrays were observed by field-emission scanning electron microscopy (FE-SEM, LEO1550). The crystal structures of the obtained samples were characterized by X-ray diffraction with graphite monochromatized CuKα radiation (BrukerD8, λ=0.15405nm). The absorption spectral characterization was performed using a Shimadzu UV-2550 spectrophotometer. Photoluminescence measurement was carried out employing a CARY Eclipse Fluorescence spectrum.

Results and Discussion

Figure 1(a)-(h) show the FE-SEM images of the ZnO nanorods arrays on zinc powder substrate with different reaction times. As shown in Figure 1(a), the zinc powders before reaction are spherical with smooth surface. The diameter of the zinc balls are in ranges of 5-12μm. Fig.1 (b), (c) shows SEM image of the ZnO nanorods successfully synthesized using Zn powder as precursor at 180 ℃ for 2h. It is clearly seen that ZnO nanorods in a hexagonal shape with the pencil shape tip have been grown on the surface of zinc balls. Most grown nanorods do not have a uniform diameter. In addition, we found after chemical etching on the surface of zinc microspheres become very rough. After a longer reaction time of 24h, high density of ZnO "dandelions" comprise numerous one-dimensional nanorods grow vertically from the substrates (Fig.1(d)-(g)).The diameter of the nanorods with the pencil shape tip is estimated to be 150-500nm. The length of the nanorods is more than 2μm. The ZnO nanorods with their –c-axes ($[000\bar{1}]$) pointing toward the center of dandelion sphere, and a large central space can be created (see a cracked opening, Fig.1(h)). In this way, ZnO dandelions with interior space had been achieved.

The XRD pattern of ZnO nanorods dandelions prepared at 180 ℃ for 24h are shown in Fig.2. The diffraction peaks are well indexed to the standard diffraction pattern of hexagonal phase ZnO (JCPDS 36-1451) with unit cell constants of a=0.3250nm, c= 0.5207nm, implying a wurtzite structure with high crystallinity. The small diffraction peak of the metallic Zn which was not reacted completely can also be seen in the Fig.2.

Figure 3 depicts the schematic illustration of formation of ZnO dandelions microspheres. Firstly, an oxide layer is formed on the surface of the metallic Zn microspheres. With increasing reaction time, Zn atoms diffuse at liquid-solid interface and then turn into soluble zincate ions ZnO_2^{2-}. At the same time, H_2 is released, which provides an additional driving force for Zn out-diffusion from the metal cores. The anions ZnO_2^{2-} react with water and deposit back to the solid phase ZnO[12]. With the continuous evacuation of Zn core, high density of ZnO nanorods grows nearly vertically from the Zn substrates. After the Kirkendall process, micrometer scale hollow ZnO dandelions organized by ZnO nanorods were formed.

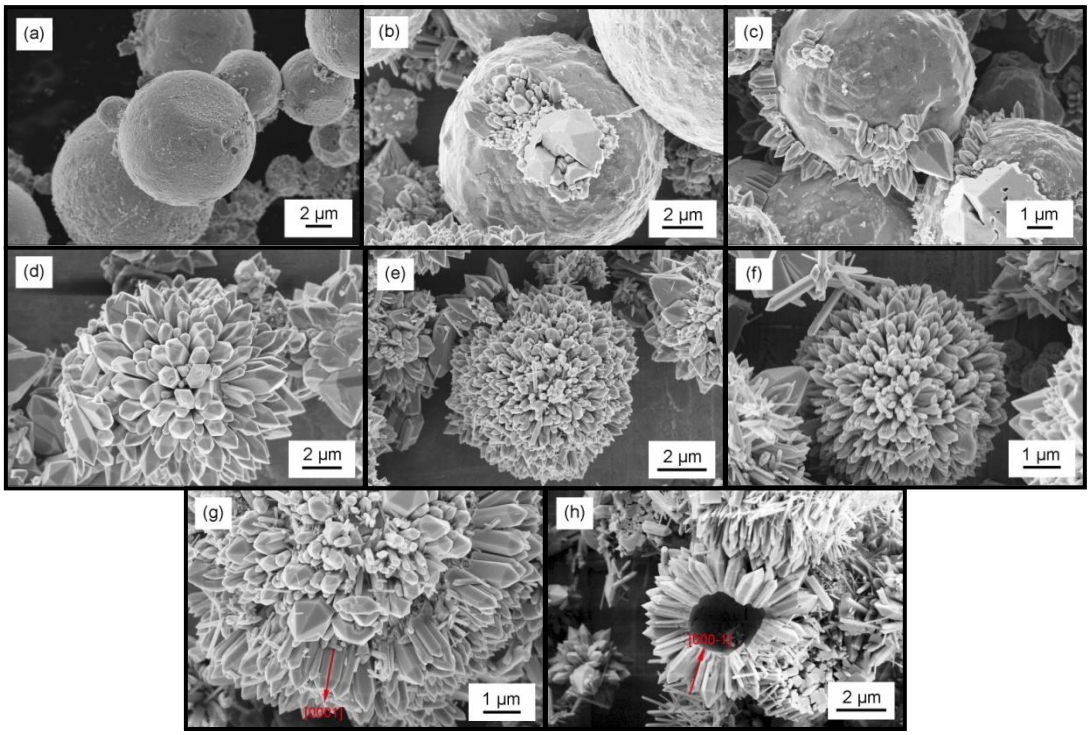

Fig.1 FE-SEM Images of ZnO Dandelions Prepared from Zn Microspheres for Different Hours: (a) The Zinc Powders before Reaction; (b), (c) 180 ℃ for 2h; (d)-(h) 180 ℃ for 24h

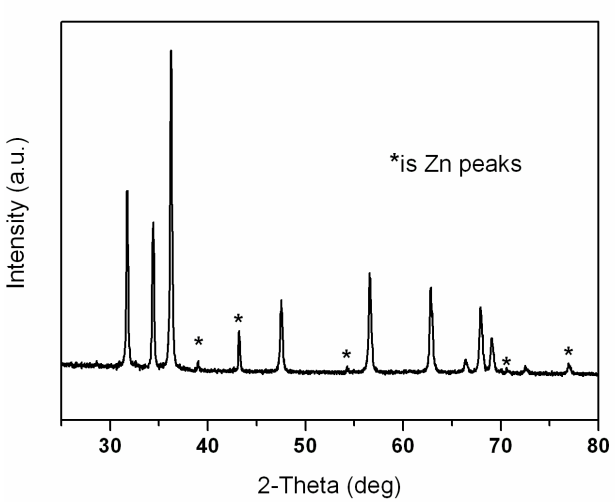

Fig.2 XRD Patterns of the ZnO Dandelions Prepared at 180 ℃ for 24h

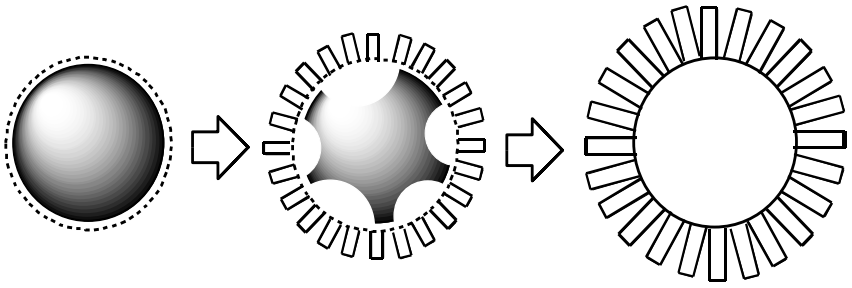

Fig.3 Schematic Illustration of Formation of ZnO Dandelions Microspheres

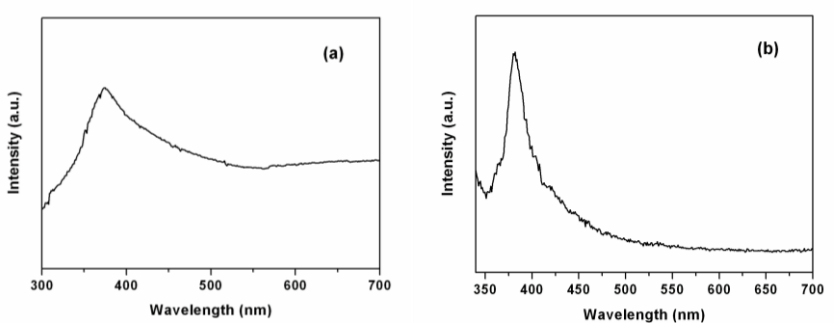

Fig.4 The Room-temperature Optical Absorption (a) and Photoluminescence Spectrum (b) of ZnO dandelions Microspheres

Fig.4(a) presents the room-temperature optical absorption of the ZnO "dandelions" by dispersing the sample in spectroscopic grade ethanol. The spectrum shown in the figure clearly indicates the excitionic character at room temperature. Generally an excitonic absorption peak appears if the defect density is considerably low. From the optical absorption spectrum it is evident that the ZnO nanorods so formed were of high optical quality.

Room temperature photoluminescence (PL) nolinebreak measurement of the as-grown ZnO nanorods was carried out by using a Xe lamp (325nm wavelength) as the source of excitation. Figure 4(b) shows the typical PL spectrum of the ZnO nanorods with a strong luminescence peak centered around 380nm. The UV emission corresponding to the near band edge emission of ZnO is attributed to the recombination of free excitons[13]. The strong room temperature UV emission property should be attributed to the high purity, good crystallinity of the as synthesized ZnO microspheres. This kind of hollow spherical ZnO structure with strong UV emission could be used in UV nano/micro-optoemission devices.

Conclusion

In summary, micrometer scale hollow ZnO dandelions organized by ZnO nanorods were formed via hydrothermal method, following a Kirkendall process. The room-temperature photoluminescence study reveals that the nanorods are of high purity and excellent optical quality, exhibiting very strong UV emission at 380nm. In principle, a lot of metal oxides and metal-semiconductor composites can be obtained in this synthetic architecture. Hopefully, they can be applied in many fields, such as light-generated electrons, three-dimensional lasing, and new photocatalysts.

References

[1] E. Kirkendall, L.Thomassen, C. Upthegrove, Mining, Metallurgical, and Petroleum Engineers, 133(1939) 186-203.

[2] A. Smigelskas, E. Kirkendall,Zinc diffusion in alpha brass, Transaction of American Institute of Mining, Metallurgical, and Petroleum Engineers.171(1947) 130-142.

[3] Y. D. Yin, R. M. Rioux, C. K. Erdonmez, et al., Formation of hollow nanocrystals through the nanoscalekirkendall effect, Science. 304 (2004) 711-714.

[4] Z.Y. Jiang, Z. X. Xie, X. H. Zhang, et al., Synthesis of single-crystalline ZnO polyhedral submicrometer-sized hollow beads using laser-Assisted growth with ethanol droplets as soft templates, Advanced Materials.16 (2004) 904-907.

[5] H. L. Xu, W. Z. Wang, Template synthesis of multishelled Cu_2O hollow spheres with a single-crystalline shell wall, AngewandteChemie International Edition, 46 (2007)1489~1492.

[6] X. X. Li, Y. J. Xiong, Z. Q. Li, et al., Large-scale fabrication of TiO_2 hierarchical hollow spheres,

Inorganic Chemistry. 45 (2006) 3493-3495.

[7] Z. Zhong, Y. Yin, B. Gates, *et al*., Preparation of mesoscale hollow spheres of TiO_2 and SnO_2 by templating against crystalline arrays of polystyrene beads, Advanced Materials. 12 (2000) 206-209.

[8] M. H. Huang, S. Mao, H. Feick, et al., Room-temperature ultraviolet nanowire nanolasers, Science.292 (2001) 1897-1899.

[9] S. C. Minne, S. R. Manalis, C. F. Quate, Parallel atomic force microscopy using cantilevers with integrated piezoresistive sensors and integrated piezoelectric actutors, Applied Physics Letters. 67 (1995) 3918-3920.

[10] Q. Wan, Q. H. Li, Y. J. Chen, et al., Fabrication and ethanol sensing characteristics of ZnO nanowire gas sensors, Applied Physics Letters. 84 (2004) 3654-3656.

[11] Y. Tian, H. B. Lu, L. Liao, et al., Synthesis and evolution of hollow ZnO microspheres assisted by Zn powder precursor, Solid State Communications. 149 (2009) 456-460.

[12] B. Liu, H. C. Zeng, Fabrication of ZnO “Dandelions” via a modified Kirkendall process. Journal of the American Chemical Society, 126 (2004) 16744-16746.

[13] K. Vanheusden, W. L. Warren, C. H. Seager, et al., Mechanisms behind green photoluminescence in ZnO phosphor powders, Journal of Applied Physics. 79(1996)7983-7990.