

Carbothermal synthesis of ZnO nanocomb structure

Y.S. Lim*, J.W. Park, S.-T. Hong, J. Kim

Corporate R&D, LG Chem/Research Park, 104-1 Moonji-dong, Yuseong-gu, 305-380 Daejeon, Republic of Korea

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Abstract

A study on the formation and characterization of ZnO nanocomb structure is presented. ZnO nanocomb was synthesized by the carbothermal reduction process with carbon black powder as a carbon source. As well as nanocomb, ZnO tetrapod and flower-like structures were also obtained in this experiment. When conventional graphite was used for a comparative study, no ZnO nanostructure could be achieved at the same experimental condition. The result shows that carbon source with large surface area more efficiently provides Zn_(g) by the enhanced solid–solid reaction between C_(s) and ZnO_(s) source materials. The resulting ZnO structures were characterized with an X-ray diffractometer (XRD), a scanning electron microscopy (SEM), and a transmission electron microscopy (TEM), and the formation mechanism of nanocomb structure was discussed.

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1. Introduction

Due to its wide band gap of 3.37 eV and a large exciton binding energy of 60 meV, ZnO has been widely investigated for optoelectronic applications [1]. Recently, various kinds of ZnO nanostructures, such as nanowire, nanorod, nanobelt, nanocomb, nanoring, nanopin, nanospring, nanohelix, and nanopropeller, were successively fabricated by numerous methods [1–6]. Among these structures, nanocomb structure has attracted much attention for the applications to nano-cantilever and nano-laser array [5,6].

The nanocomb structure can be described as a self-organized single-crystalline multi-dimensional nanostructure, consisting of one-dimensional nanowires and two-dimensional nanosheet. ZnO nanocomb structure can be synthesized by carbothermal reduction process between graphite carbon and ZnO powder. However, because high Zn_(g) vapor pressure is essential to grow the ZnO nanocomb structure, high temperature process (1350–1500 °C) and/or precise gas control system had been required for the carbothermal reduction [7–9].

Recently, there were challenges to control the Zn_(g) vapor pressure by using other sources rather than the mixture of ZnO and graphite powder [9–12]. Gundiah et al. [11] reported that

the ZnO nanowire could be obtained by the carbothermal reduction of ZnO or zinc oxalate with graphite or multi-walled carbon nanotube at 900 °C, and Yu et al. [12] showed that the high-yield Zn_(g) vapor could be produced by using zinc carbonate source rather than ZnO powder. Moreover, Leung et al. [9,10] successfully controlled the Zn_(g) vapor pressure by using novel carbon sources, such as single-walled carbon nanotube (SWCNT), multi-walled carbon nanotube, and C₆₀. They synthesized ZnO nanocomb at relatively low temperature (1000–1100 °C) by using SWCNT as a carbon source material [9]. Because the growth of ZnO nanostructure is strongly dependent on the vapor pressure, proper control of the process is of great importance for the fabrication of various novel ZnO nanostructures.

In this work, we synthesized large quantity of free-standing ZnO nanocomb by the carbothermal reduction process at 1050 °C with a carbon black powder as a carbon source. As well as the nanocomb structure, ZnO tetrapod and flower-like structure were also fabricated with the carbon black source. Carbon black is a cheaper and more abundant material than SWCNT, and it has a larger surface area ($A_s = 30\text{--}1600\text{ m}^2/\text{g}$) than graphite ($<10\text{ m}^2/\text{g}$). Due to its large surface area, the reduction of ZnO source was more efficiently enhanced so that we could synthesize the ZnO nanocomb structure at relatively low temperature without any additional gas control system. When conventional graphite carbon source was used for a comparative study, no ZnO nanostructure could be achieved at the same experimental condition. With these results, it was confirmed that the reducing

* Corresponding author.

E-mail address: yslim@lgchem.com (Y.S. Lim).

power of $\text{ZnO}_{(s)}$ source into $\text{Zn}_{(g)}$ vapor is strongly dependent on the surface area of carbon source, and that the fabrication of ZnO nanocomb can be performed more efficiently by using carbon source of large surface area.

2. Experimental details

ZnO nanostructure was prepared with a fixed amount of the mixture of high purity ZnO powder (0.2 g) and carbon powder (0.05 g). For a comparative study, graphite ($A_s = 3 \text{ m}^2/\text{g}$) and carbon black powder ($A_s = 800 \text{ m}^2/\text{g}$) were used as the carbon source. The surface areas of the carbon sources were measured by Brunauer–Emmett–Teller (BET) method. The carbon powder was mixed with ZnO powder, ground by mortar and pestle, and loaded on a platinum boat. The platinum boat was placed at the closed end of a fused-silica tube (diameter = 2 cm, length = 12 cm), and Au-catalyzed Si substrate was also loaded with the distance range of 0–10 cm from the source materials. The Au-catalyzed Si substrate was prepared by ion beam sputtering method, and the thickness of Au was $\sim 5 \text{ nm}$. The fused-silica tube was inserted into a horizontal tube furnace, having a temperature gradient (maximum temperature = $1050 \text{ }^\circ\text{C}$, minimum temperature = $515 \text{ }^\circ\text{C}$). The temperature was measured by K-type thermocouple. The source material in the platinum boat was heated up to $1050 \text{ }^\circ\text{C}$ with a heating rate of $\sim 16 \text{ }^\circ\text{C}/\text{min}$ in air without any carrier gas. Therefore, the vaporized $\text{Zn}_{(g)}$ during the carbothermal reduction between ZnO and carbon source powder was transferred to the substrate at low temperature region simply by the temperature gradient in the fused-silica tube. When carbon black powder was used, 30 min of heat treatment resulted in the production of ZnO nanocomb structure. In addition to the nanocomb, other kinds of ZnO structures, such as flower-like and tetrapod structure were also fabricated. However, with the graphite carbon source, no ZnO nanostructure was produced. The ZnO structures were characterized with an X-ray diffractometer (XRD), a scanning electron microscopy (SEM), and a transmission electron microscopy (TEM). XRD analysis was conducted on a Bruker D4 Endeavor with Cu K α radiation operating at 40 kV and 40 mA. SEM analysis was performed with a Hitachi S-4800 scanning electron microscope, operated at 15 keV for secondary electron imaging, and TEM characterization was performed with a JEOL JEM-ARM1300S high-voltage transmission electron microscope (HVEM), operated at 1250 keV.

3. Results and discussion

Fig. 1(a) and (b) show SEM micrographs of nanostructures synthesized by using graphite and carbon black as the starting materials, respectively. As shown in Fig. 1(a), with the graphite carbon source, no ZnO nanostructure was produced within the temperature range of $950\text{--}1000 \text{ }^\circ\text{C}$. But, only Au nanoparticles (size = $10\text{--}50 \text{ nm}$) could be observed on the substrate. Some white products were deposited on the inner surface of the fused-silica tube just above the platinum boat, but they could not be observed at any other region in the tube.

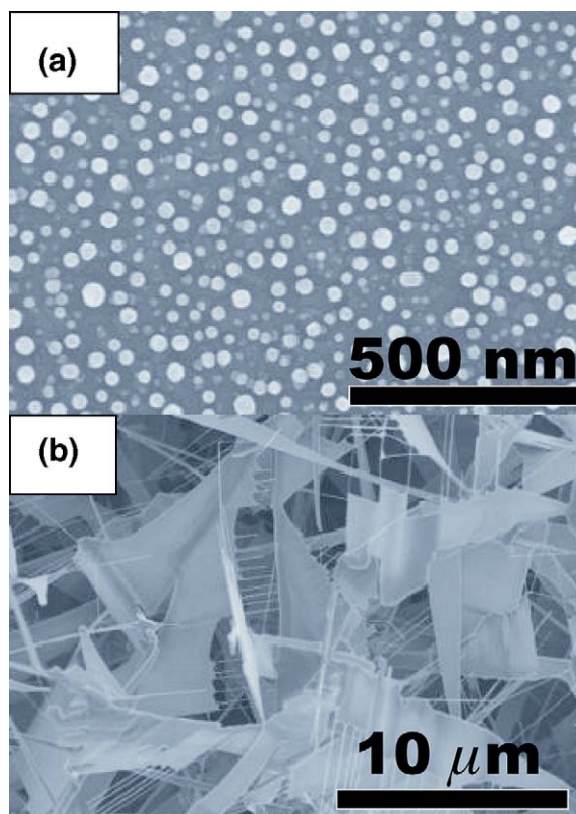


Fig. 1. SEM micrographs of (a) Au nanoparticles and (b) ZnO nanocomb, resulting from the carbothermal reduction by using graphite and carbon black source, respectively.

In literature, there are many reports on the ZnO nanostructure grown by using graphite as carbon source under Ar and/or O_2 carrier gas flow [1,13]. However, in this experiment, we did not use any carrier gas so that vaporized $\text{Zn}_{(g)}$ could be transferred to the substrate only by the temperature gradient in the fused-silica tube. Moreover, to maximize the effect of carbon source, we intentionally suppressed the carbothermal reduction of ZnO powder into $\text{Zn}_{(g)}$ by using small amount of carbon source (only 20 wt.% in the mixture). Therefore, the supply of $\text{Zn}_{(g)}$ by using graphite source was not sufficient for the growth of ZnO nanostructure in this experimental condition.

On the other hand, with the carbon black source, large quantity of free-standing nanocomb was synthesized, as shown in Fig. 1(b). Considering both experiments performed at the same condition except for the carbon source, these results indicate that the surface area of carbon black powder acts a certain role. For the formation of ZnO nanocomb structure, high $\text{Zn}_{(g)}$ vapor pressure should be provided during the carbothermal reduction process. However, as shown in Fig. 1(a), this experimental condition is very harsh to the reduction of ZnO powder into $\text{Zn}_{(g)}$. Therefore, it is evident that the carbon black powder with a large surface area can enhance the solid–solid reaction between ZnO and carbon source so that it can vaporize $\text{Zn}_{(g)}$ more efficiently than graphite carbon source [14].

In addition to ZnO nanocomb, using the carbon black powder resulted in other kinds of ZnO structure at lower substrate temperature. Fig. 2(a) is a SEM micrographs of free-standing ZnO

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