

GROWTH AND SIZE CONTROL OF ZnO NANOTETRAPODS PREPARED BY CURRENT HEATING TECHNIQUE

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Abstract

In this research, the growth and morphologies of zinc oxide (ZnO) nanotetrapods were revealed and characterized. The ZnO nanotetrapods were synthesized by using current heating technique. First, zinc rod was prepared with a diameter of 6 mm and a length of 10 mm by mixing zinc powder and polyvinyl alcohol (PVA) solution of 1% by weight and heat at 400°C for 3 h. Then, the direct current of 20-60 A were applied to the zinc rod for heat and cause to oxidation reaction to form ZnO. XRD and FE-SEM results were showed that the product was wurtzite hexagonal structure of ZnO tetrapod with the average size of particles of 40-200 nm. In growth situation, the activated plasma time duration was about 2-10 sec and the distance between plasma and substrate was set to 5.0-12.5 cm. The results were showed that the size of ZnO nanotetrapod were depended on two parameters, the distance between the plasma and substrate and the duration time of reaction. Finally, the growth mechanism of ZnO nanotetrapods was proposed and realized.

Keywords: ZnO, tetrapods, nanostructure, growth mechanism, current heating

Introduction

Zinc Oxide (ZnO) is one of a metal oxide wide-bandgap semiconductor, which is normally used for many applications such as for semi-conducting, photo-conducting, solar cell, piezoelectric, or gas sensor, etc. (Duan and Lieber, 2000; Wan *et al.*, 2004). It has a hexagonal close-packed structure (Wurtzite type) with an energy band gap of 3.37 eV and can be synthesized by various techniques, which has a variety of shapes in the nanometer-scale for example, nanoparticle, nanowire, nanobelts nanotetrapod, etc. (Dai *et al.*, 2003).

The effect of nanostructures effect on ZnO has got great interest, especially in the gas sensor application. Usually, the gas sensing properties of ZnO strongly depend on the surface of the materials due to a very large surface-to-volume ratio. There are expected to detect sensing gas molecules at lower concentration (Chen *et al.*, 2006; Hongsith *et al.*, 2010). Moreover, when the sensors which having particle size very close to the value of Debye length ($2L_d$), exhibited the ultrahigh sensitivity and have possibility to detect for a ppb level of gas

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concentration. It was suggested that the ultra-high sensitivity is revealed when the particle size is close to 15 nm (Li *et al.*, 2007; Hongsith *et al.*, 2010).

The tetrapod shape of ZnO has presently gained attraction due to its properties. Typically, ZnO nanotetrapods can be simply synthesized by using the thermal oxidation reaction technique (Uchida *et al.*, 2015). From previous work (Hongsith *et al.*, 2009), the growth kinetics and characterization of ZnO tetrapod were explained. The growth model of ZnO tetrapod could be explained by the kinetics of anisotropic growth via a vapor-solid mechanism with a three-dimension (3D) tetrahedral nucleus as a seed. In detail, the 3D tetrahedral nuclei forms by accumulation and then condensation of ZnO vapor due to supersaturation conditions. These 3D nuclei grow along the c-axis in each direction of tetrahedral axes due to symmetrical structure, finally forming the four-legged structure of ZnO tetrapod.

However, the synthesis of ZnO nanotetrapod has still challenge (Iwanaga *et al.*, 1993; Ronning *et al.*, 2005; Uchida *et al.*, 2015), it is difficult to control the size of tetrapod due to difficult to control the mixing of zinc vapor and oxygen gas, difficult to control oxidation temperature, difficult to control the supersaturation conditions and especially difficult to obtain the uniform ZnO tetrapod particles. Therefore, to synthesize uniform ZnO tetrapod, the mixing of zinc vapor and oxygen gas, oxidation temperature and the supersaturation conditions were focused.

ZnO nanotetrapod can be synthesized by various growth techniques (Thepnurat *et al.*, 2015). One of an exciting technique is a current heating, that is a simple, low-cost and based on an oxidation reaction at high temperature (Sivakumar *et al.*, 2012). The plasma temperature was simply controlled by varies the apply current.

In this research, the growth and morphologies of ZnO nanotetrapods were revealed and characterized. ZnO nanotetrapods were synthesized by using current heating technique, which applied the direct current of 20A-60A. The product on the substrates and yield were collected and calculated, respectively. The shape and size of the products are confirmed by means of FE-SEM. In growth situations, the activated plasma time duration and the distance between plasma and substrate were controlled. Finally, the growth mechanism of ZnO nanotetrapods was proposed and realized.

Materials and Methods

ZnO nanostructures and ZnO nanotetrapods were synthesized by the current heating technique. First, the zinc rod was prepared with a diameter of 6 mm

and a length of 10 mm by compressing the mixing of zinc powder and polyvinyl alcohol (PVA) solution with a concentration of 1% by weight and heat the rod at 400°C for 3 h. The zinc rod after heat was showed in Figure 1. Then, the direct current of 20A were applied to the zinc rod for heat and cause to oxidation reaction to form ZnO. When the current was applied, the plasma was immediately activated. The white fogs were produced inside a chamber and turned to wool-like products. The plasma-activated and products were showed in Figures 1(b) and 1(c), respectively.

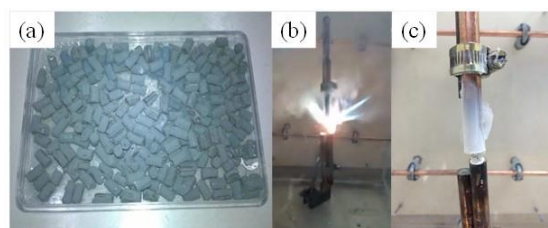


Figure 1. (a) zinc rod with a diameter of 6 mm and a length of 10 mm were prepared by mixing zinc powder and polyvinyl alcohol (PVA) solution of 1% by weight and heat at 400°C for 3 h. (b) and (c) the plasma-activated and products, respectively

The ZnO products were collected on the filter paper as a filter layer in the vacuum cleaner for calculation the yield production of synthetization. The method was repeated by increasing the current to 25A, 30A, 35A, 40A, 45A, 50A, 55A, and 60A, respectively. Particle size analysis of ZnO products was determined by measuring the random changes in the intensity of light scattered from a suspension of ZnO in ethanol. This technique is commonly known as Dynamic Light Scattering (DLS). The products were characterized by using a field emission scanning electron microscopy (FE-SEM) for morphology, and an X-rays diffractometry (XRD) and transmission electron microscopy (TEM) for crystal structure. Finally, the growth mechanism of ZnO nanostructures and ZnO nanotetrapods was proposed and realized.

Results and Discussion

ZnO Morphology

Figure 2(a) was the size distribution curve of ZnO products. The results were showed that two range of size were observed. The smaller diameter size of products had range of 155-245 nm and the bigger range of 360-1,100 nm. The optical microscope image of ZnO products obtained on filter paper substrate from the current heating was

showed in the inset of Figure 2(a). The white layer as a powder was observed indicating some nanostructures.

Figure 2(b) showed the X-ray diffraction pattern (XRD) of the ZnO products on the filter paper. It had been shown that all diffraction peaks could be indexed as a hexagonal ZnO wurtzite structure with corresponding to JCPDF file number 89-1,397, space group P63mc with the lattice constants of a-axis about of 3.2 Å and c-axis of 5.2 Å. In addition, there was no peak of zinc metal or other phases of ZnO. It was confirmed that the zinc was clearly transformed into ZnO by the current heating technique.

Mass of ZnO products were measured and then calculates for Yield production by using an equation of

$$Yield(\%) = \frac{m_{ZnO}}{m_{Zn}} \times 100\% \quad (1)$$

where m_{ZnO} is mass of ZnO products and m_{Zn} is mass of zinc rod. Yield product of ZnO nanostructure for different apply current were calculated and displayed in Table 1. Yield product was increased when increasing apply current, however, the optimize yield product was exhibited in range of 40-50A.

The morphologies of the ZnO products which selected apply current of 20A, 40A and 60A was shown by FE-SEM images in Figure 3(a)-(c), at magnification x10,000. The morphologies of the ZnO products was not clearly different. However, ZnO tetrapod with the average size of particles of 40-200 nm.

Particle Size Control

To control the size of ZnO nanotetrapods, in growth situations, the parameter TD as activated plasma time duration and DS as the distance between plasma and substrate were focused. DS was fixed to 12.5 cm, 10.0, 7.5 cm, and 5.0 cm, respectively and TD was set to 10 sec. The products obtained from the synthesis were showed in Figure 4. Comparison from Figures 1(b) and 1(c), the DS was measured from the center of plasma in

horizontal plane. Figure 4(a) was FE-SEM image of the ZnO nanotetrapods which collected at DS equal to 12.5 cm. The small tetrapod was displayed, which had average size about less than 100 nm.

Next, the parameters DS was fixed at 10.0, 7.5, and 5.0 cm, respectively, and TD was not changed. The ZnO product obtained from the synthesis was ZnO nanotetrapods which had a longer leg and bigger than before as shown in Figure 4(b)-(d), respectively. In this experimental condition, these results were indicated that ZnO nanotetrapod should be grown up with 5.0- to 12.5 cm of DS to generate ZnO nanotetrapods. The longer of DS was the

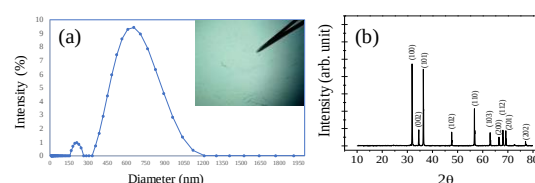


Figure 2. (a) size distribution analysis and the inset figure of microscope image of ZnO products on the filter paper and (b) the XRD pattern of the ZnO products

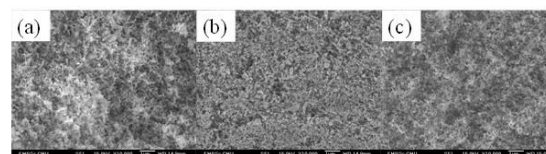


Figure 3. FE-SEM images of the ZnO products with (a)-(c) was 20A, 40A and 60A, respectively

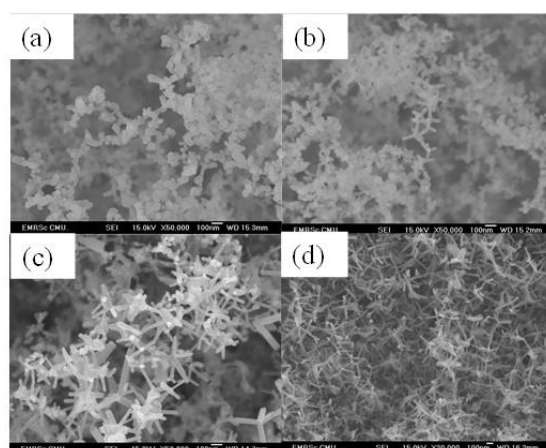


Figure 4. FE-SEM images of the growth evolution of ZnO nanotetrapods in parameter of the distance between the plasma and substrate when (a) - (d) was 12.5, 10.0, 7.5, and 5.0 cm with plasma time duration of about 10 s, respectively

Table 1. Yield product of ZnO nanostructures was prepared by current heating technique

Current (A)	Yield (%)	SD	Error (±)
20	9.00	1.46	0.65
25	10.03	2.71	1.21
30	13.92	2.15	0.96
35	17.22	1.96	0.88
40	19.97	5.15	2.31
45	20.32	1.32	0.59
50	18.49	4.01	1.79
55	14.38	3.78	1.69
60	12.78	3.01	1.34

smaller and shorter leg of tetrapod due to the growing evolution of ZnO nanotetrapods.

Growth Mechanism

Normally, the growth mechanism of the belt-like, wire-like nanostructures can be explained by the kinetics of anisotropic growth via a vapor-solid mechanism. The nucleation probability P on the surface of a nanostructure is given by (Dai *et al.*, 2003; Choo-pun *et al.*, 2008, 2010; Hong-sith *et al.*, 2009)

$$P = B \exp\left(\frac{-\pi\sigma^2}{k^2T^2 \ln(\alpha)}\right) \quad (2)$$

where B was a parameter constant, σ was the surface energy of the solid tetrapod, k was the Boltzmann's constant, T was the absolute temperature, and α was the supersaturation ratio between the actual vapor pressure and the equilibrium vapor pressure corresponding to temperature T (usually, $\alpha > 1$).

From previous report on the growth mechanism of ZnO tetrapod (Hong-sith *et al.*, 2009), the growth of wire-like or belt-like nanostructures based on the equation of nucleation probability was explained in the term of the different supersaturation ratio. However, the growth mechanism of the tetrapod was three-dimensional growth kinetics. From Equation 2 at the same supersaturation ratio, the lowest surface energy as σ_{min} was suggested that the highest nucleation probability P .

The bright field TEM image of ZnO tetrapods and corresponding selected-area diffraction pattern (SADP) were showed in Figures 5(a) and 5(b), respectively. The results were showed that the growth direction of the leg of tetrapod was along c-axis with index of [0001] direction. However, according to the structure of ZnO, the growth direction of a one-dimensional nanostructure was normally along a low crystal index for example [0001], $[10\bar{1}0]$, $[11\bar{2}0]$, etc (Shan *et al.*, 2004; Newton *et al.*, 2007). This is due to their surface energy which is related to the crystal plane index in crystal structure. Truly, the [0001] c-axis direction of ZnO had the lowest surface energy (Shan *et al.*, 2004). Therefore, the c-axis of the ZnO structure exhibited the fastest growth rate and the highest possibility for the growth direction.

For the growth evolution of ZnO tetrapod, first, the tetrahedral structure as 3D nucleation was performed (Ronning *et al.*, 2005; Hong-sith *et al.*, 2009). It was four grains of ZnO structures as a starting nucleus following the Ronning mode (Ronning *et al.*, 2005). The evidence of this model was confirmed by the FE-SEM image as shown in Figure 6(a). The nanoparticle look-like the ZnO

nucleation was exhibited. The inset image in Figure 6(a) showed the morphology of the nucleation, the nucleation size was about 100 nm. Next, the 3D structure can form by accumulation and then condensation of ZnO vapor due to supersaturation conditions, growing along the c-axis and becomes four legs structure of tetrapod as shown in Figure 6(b). However, the continued condensation of ZnO vapor was still occurred due to supersaturation conditions, the structure becomes bigger and longer legs structure of tetrapod, according to FE-SEM image as shown in Figures 6(c) and 6(d), respectively.

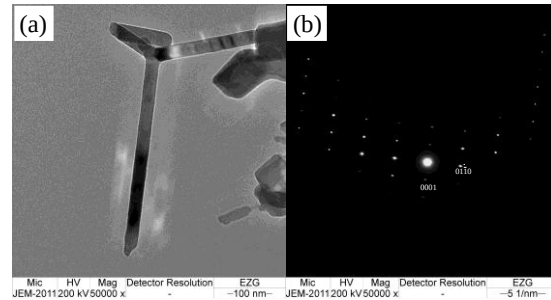


Figure 5. (a) Bright field TEM images of a ZnO tetrapod and (b) with corresponding SADP

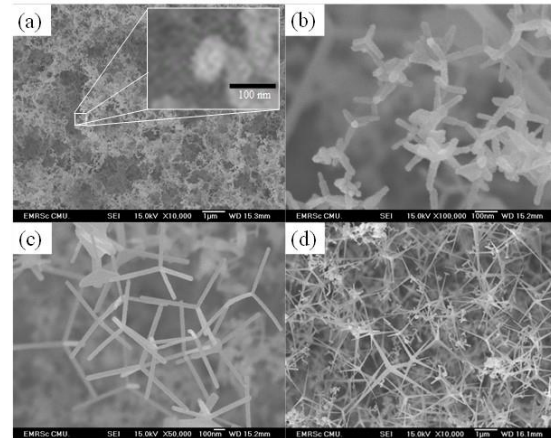


Figure 6. (a) FE-SEM images of ZnO nucleation and the inset image in (a) was zoom in of nucleation. (b)-(d) FE-SEM images of the crystal growing of ZnO nanotetrapods depending on the duration time of synthesis

Finally, the ZnO products obtained from the current heating technique, the longer DS over 12.5 cm as a white fog, the ZnO products were the nanoparticles with average size less than 100 nm, which confirmed by SEM image as shown in Figure 2. However, in the range of DS equal to 5.0-12.5 cm, it was indicated that the products were the tetrapod-like structures. It was explained by the parameter

α in Equation 2 because the high α was found near the plasma region resulting in high nucleation probability. This evidence was confirmed by the morphology of the product, the longer distance between plasma and substrate result in a shorter leg structure of ZnO tetrapod. The size of tetrapod depended on the distance between the plasma and substrate as a DS parameter. The leg length of ZnO tetrapod could be controlled. The small size of nanoparticles and nanotetrapods had a high potential application for ultra-high sensitivity of gas detectors (Hongstith *et al.*, 2010).

Conclusions

We have successfully synthesized ZnO nanostructures and ZnO nanotetrapods by using current heating technique. The average size of nanoparticle particles of 40-200 nm. The crystal growth of nanostructures was explained via the size evolution of crystal. There were depended on two parameters, the distance between the plasma and substrate and the duration time of reaction.

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