Materials Sciences and Applications, 2014, 5, 193-198
Published Online March 2014 in SciRes. http://www.scirp.org/journal/msa
http://dx.doi.org/10.4236/msa.2014.54024

Synthesis of Zirconia Oxide (ZrO_2) Nanofibers on Zirconnia Substrates by Ultrasonic Spray Pyrolysis

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Received 31 December 2013; revised 6 February 2014; accepted 27 February 2014

Abstract

Zirconia oxide (ZrO_2) nanofibers were synthesized using Phosphorus/water mixture as catalyst by ultrasonic spray pyrolysis CVD on the zirconia substrate at 900˚C for 1 h in N_2 gas. Scanning electron microscopy (SEM) and high-resolution transmission electron microscopy (HRTEM) examinations show that all the synthesized nanofibers have uniform surface morphology and their diameters are in the range of 100 nm. The HRTEM selected-area electron diffraction pattern (SAED) shows that crystalline ZrO_2 phase exist in the nanofibers, and the energy-dispersive x-ray spectroscopy (EDS) results show that the elements of Zr and O are uniformly distributed across the nanofiber matrix. The phosphorus atoms corroded the entire Zirconia substrate surface, and the Zirconia-Phosphorus liquid-catalyzed the solid-liquid-solid mechanism is proposed to explain the growth of the nanofibers.

Keywords

Nanofibers; Chemical Vapor Deposition; EDS

1. Introduction

In recent years, the many important works are then published in which a chemical vapor deposition (CVD) is introduced and successfully synthesized in the nanofibers or nanorods of ZnO [1], SnO_2 [2], CaN [3], TiO_2 [4] and Bi_2O_3 [5] etc. They are a type of one-dimensional (1-D) nano-structural materials exhibit novel physical proper-

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How to cite this paper: Zhang, J.H., *et al.* (2014) Synthesis of Zirconia Oxide (ZrO_2) Nanofibers on Zirconnia Substrates by Ultrasonic Spray Pyrolysis. *Materials Sciences and Applications*, **5**, 193-198. http://dx.doi.org/10.4236/msa.2014.54024

ties in a number of areas [6]. They have been widely studied due to the great potential applications in electronic properties [7], and excellent optical properties [8]. Among which the ZrO_2 nanofibers have a high aspect ratio and a high specific surface area, the nanofibers have been extensively applied in excellent thermal and chemical stability, high strength and fracture toughness, low thermal conductivity, high corrosion resistance, because of its technical importance and broad practical applications, such as thermal barrier coatings [9], solid oxide fuel cells [10], various sensors [11], gate dielectrics [12], catalysts [13], ceramic biomaterial [14], metallic glass [15]. Several methods have been used to synthesize ZrO_2 nanofibers, including ionic-liquid route [16], a modified sol-gel method [6], electrospinning [17]. However, there have been no reports on the ZrO_2 nanofibers using CVD method.

In the present study, we have obtained nanofibers that have diameter of about 100 nm with using phosphorus/water mixture as catalyst. This method produces mist of phosphorus/water mixture by ultrasonic spray pyrolysis for the synthesis of nanofibers. A possible growth mechanism of such ZrO_2 nanofibers is also discussed in the present study, e.g. the growth of such nanofibers is attributed to solid-liquid-solid (SLS) growth mechanism [18]. This is the promising method to grow ZrO_2-nanofibers.

2. Experimental

Details of the present method have been reported previously as shown in **Figure 1** [18]. A zirconia substrate was used as a substrate and the mixture of phosphorus/water or water was used as corrosive source. The reactor furnace was heated to the range of 700˚C - 1000˚C in N_2 flow, the phosphorus mixed with the water or only water was placed inside the atomization chamber of the ultrasonic spray pyrolysis machine [19]. The synthesis was in N_2 gas atmosphere. In the present study, phosphorus (Kojundo Chemical Laboratory; 99%) was used. Produced samples were analyzed using a scanning electron microscope (SEM), a transmission electron microscope (TEM), as well as energy dispersive spectrum (EDS).

3. Results and Discussion

Figure 2(a) shows SEM image of ZrO_2 nanofibers that were synthesized on the zirconia substrate at 900˚C for 1 h, they were uniform and their diameter was about 100 nm, disordered vertically condition. We found that the present an individual nanofiber having a diameter of about 100 nm, a black spot on the tip of nanofiber by the TEM observations which is shown in **Figures 2(b)** and **(c)**. The TEM observation indicates that the present bulky bottom of nanofiber as shown in **Figure 2(d)**, it indicated that the nanofibers of growth from the zirconia substrate. We also observed a black spot at the tip of nanofiber. **Figure 2(e)** shows the EDS spectrum of the tip (spot (i)) of nanofiber shows three distinct peaks of Cu, O and Zr, with the Cu peak possibly coming partially from the TEM grid. However, we did not find any phosphorus in the tip of nanofiber within the detection limits.

The short and sparse nanofibers was observed in the sample synthesized at 700˚C as shown in **Figure 3(a)**. The yield of nanofibers can be synthesized at 800˚C, the length of nanofibers nearly did not change as shown in **Figure 3(b)**. Straight and longer nanofibers yield were observed in the sample synthesized at 900˚C as shown in **Figure 3(c)**. At 1000˚C, the density of nanofibers became sparse again, and the aggregation of the bottom of nanofibers originated from the surface of zirconia substrate. According to above these SEM images, we expected that the growth temperature can affect the synthesis of nanofibers. The amounts of active zirconia/phosphorus

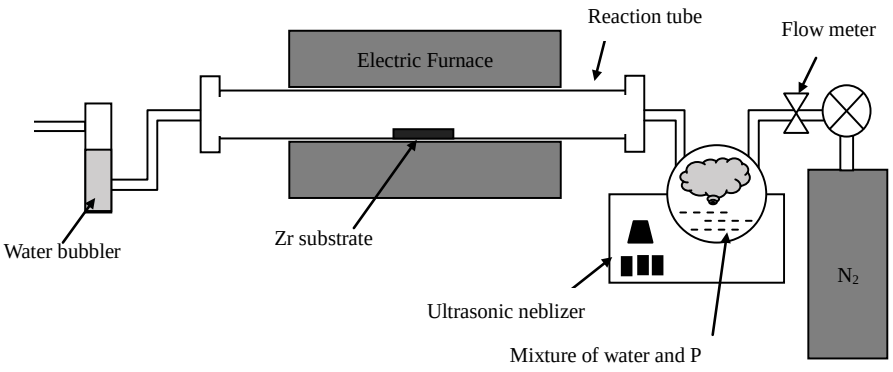

Figure 1. Schematic image of the apparatus of the spray pyrolysis CVD.

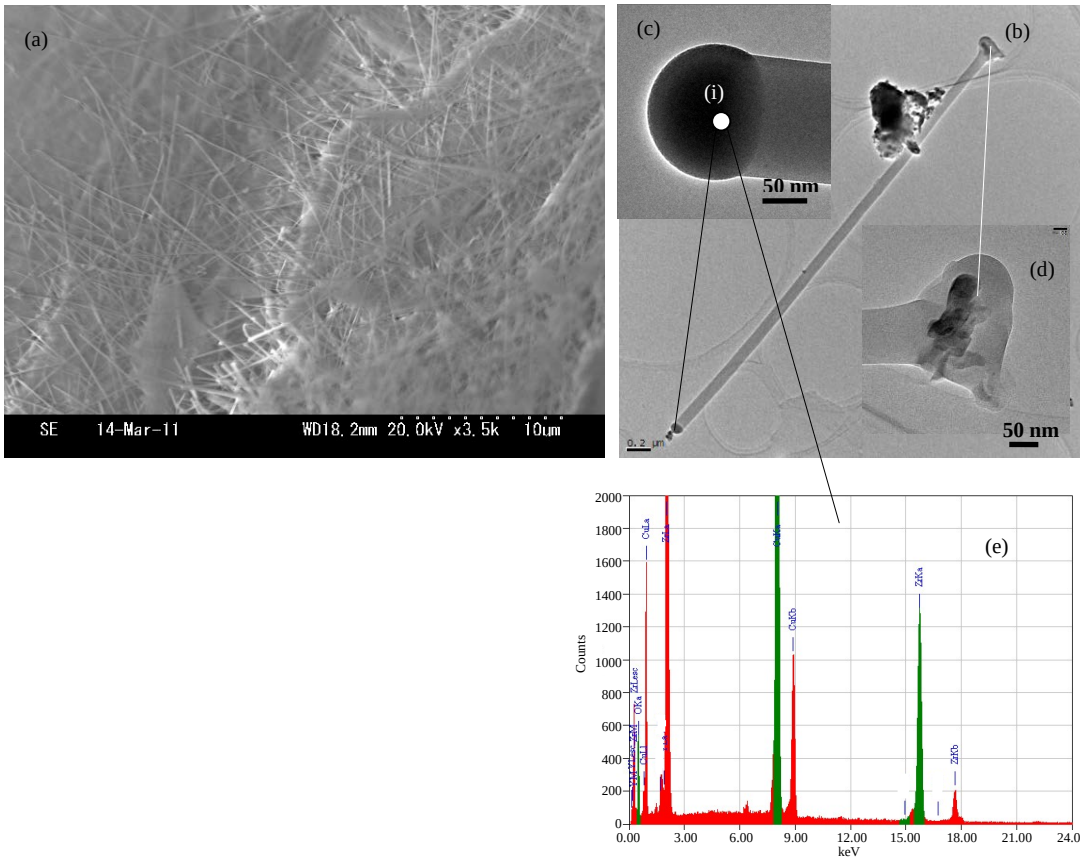

Figure 2. SEM images of ZrO_2 nanofibers on Zr substrate synthesized at 850˚C. (a) SEM image of nanofibers; (b) TEM image of nanofiber; (c) The TEM image of nanofiber tip; (d) The TEM image of nanofiber bottom; and (e) The EDS of nanofiber tip.

mixture increase with increasing growth temperature. However, the aggregation of the bottom of nanofibers are prompted by higher temperature heating, as shown in **Figure 3(d)**. It is worth pointing out that the calcination at 900˚C resulted in some substantial the ZrO_2 nanofibers morphology as compared to synthesis at 700˚C, 800˚C, 1000˚C.

Figure 4(a) shows a TEM image of nanofiber body, many little particles were adsorbed on the surface of the body, due to evaporation of the polymer and the crystallization of ZrO_2, that was composed of nanocrystalline grains <5 nm in size. The inset shows the electron diffraction pattern of selected area. The rings were indexed as the (111), (200), (220) and (311) lattice planes as shown in **Figure 4(b)**. **Figure 4(c)** shows the EDS of the body (spot (ii)) of the nanofiber. The Cu, Zr and oxygen elements are detected, respectively. The Cu peak results from the Cu parts of the measurement chamber and the Zr and O peaks comes from the body of nanofiber. However, we found that the phosphorus element cannot existed in the nanofibers, and we estimated that flow N_2 gas can carry phosphorus element away from the nanofibers owing to the high temperature.

Figure 5 is a schematic illustration of the growth mechanism. It involved in the formation of the ZrO_2-nanofiber are proposed as follows. Initially, the phosphorus coating on the zirconia substrate forms a thin phosphrous film, as illustrate in **Figure 5(a)**. When the reaction temperature increases, the zirconia substrate is oxidized in the carrier N_2 and by the water. A reaction between the Zr and P occur form a thin Zr-P eutectic liquid layer, as illustrated in **Figure 5(b)**. Because the melting point of Zr is 1855˚C, a temperature at which the Zr vapor phase is negligible, and the Zr substrate itself serves as an Zr source without and additional external Zr source, the nanofibers should be formed via a solid-liquid-solid (SLS) mechanism. Finally, the surface of the Zr-P eutectic liquid soon becomes supersaturated, and appeared the aggregating into ZrO_2-nanoparticles condition via heating as shown in **Figure 5(c)**. And then the nanofibers precipitate out and continue to grow from ZrO_2-nanopaticles (saturation nucleation) of this supersaturated surface as illustrate in **Figure 5(d)**, possibly through the oxidation

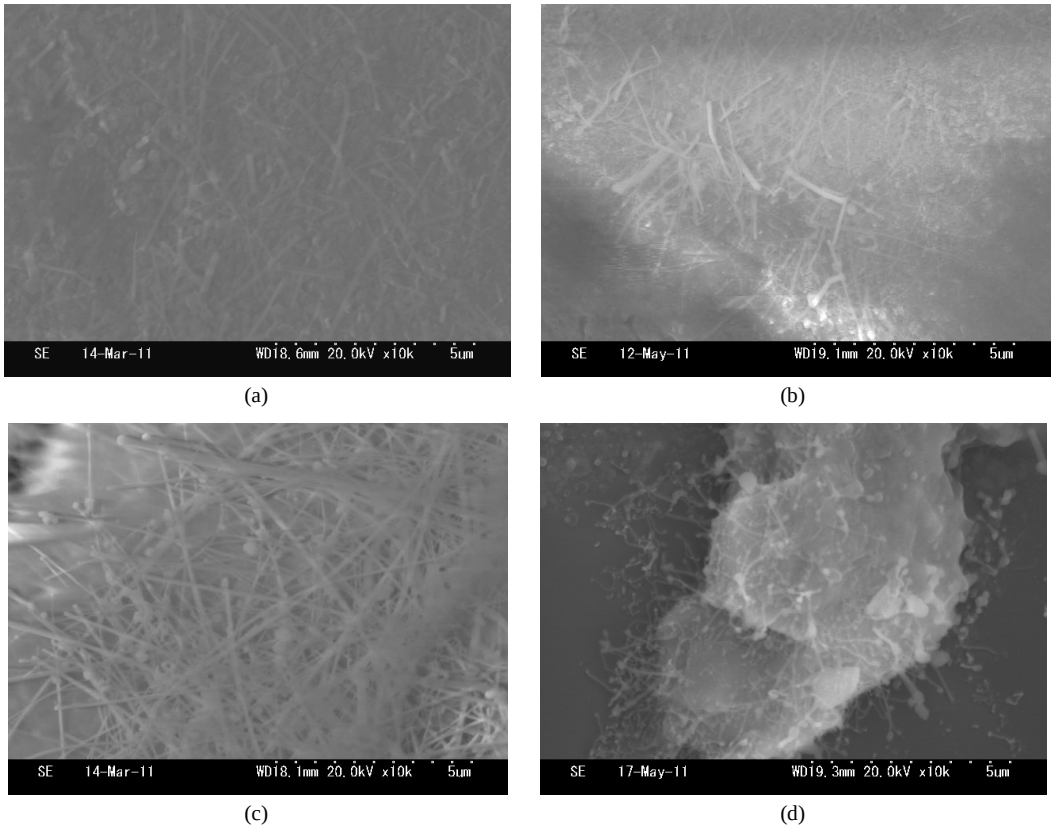

Figure 3. SEM images of nanofibers synthesized from different temperatures: (a) 650˚C; (b) 750˚C; (c) 850˚C; (d) 950˚C.

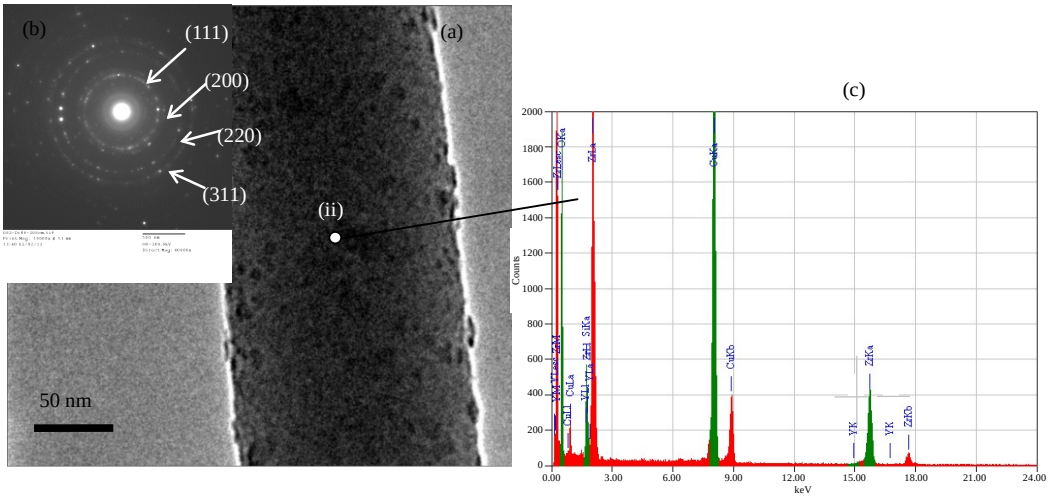

Figure 4. (a) TEM images of nanofiber body; (b) EDS spectrum of TEM image of a nanofiber; (c) EDS of nanofiber.

reactions of $Zr + 2H_2O \rightarrow ZrO_2 + 2H_2$.

4. Conclusion

In the present study, we successfully synthesized the nanofibers with a mixture of phosphorus/water on a Zr substrate using ultrasonic spray pyrolysis method. The ZrO_2 nanofibers were produced on the surface of the Zr

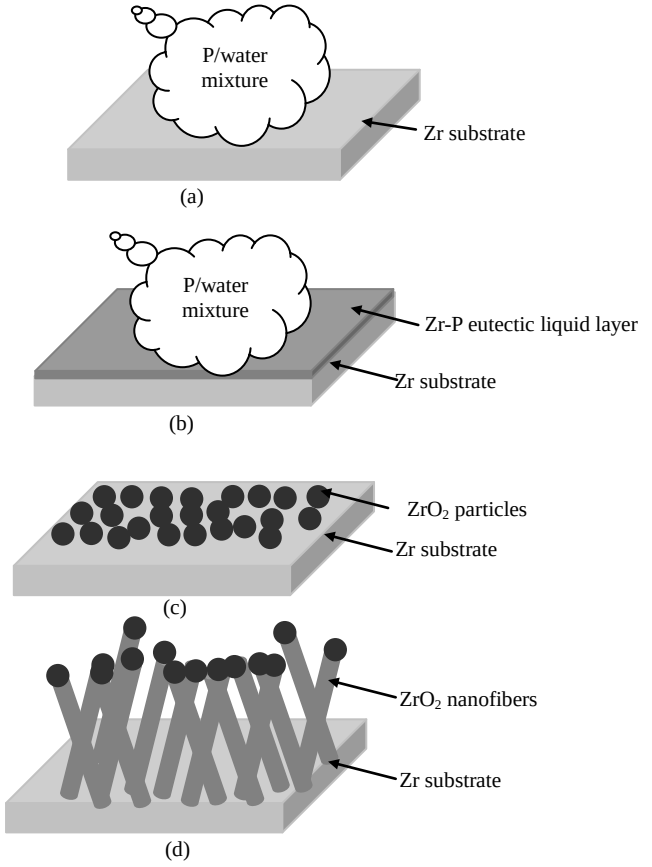

Figure 5. Schematic illustration of the growth processes.

substrate, and the mixture of Zr/phosphorus eutectic liquid layer thereafter the synthesized nanoparticles on Zr substrate played a key role in determining the growth model of nanofibers. A possible mechanism for this process is the formation of the nanofibers from the surface the Zr-P liquid layer. We believed that this approach to the synthesis of nanofibers may be further used in the fabrication of fuel cells and oxygen sensors.

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