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# Facile fabrication of forest-like ZnO hierarchical structures on conductive fabric substrate

**Yeong Hwan Ko, Sunkook Kim, Wook Park, and Jae Su Yu***

Department of Electronics and Radio Engineering, Institute for Laser Engineering, Kyung Hee University, 446-701 Yongin, Republic of Korea

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* Corresponding author: e-mail jsyu@khu.ac.kr, Phone: +82 31 201 3820, Fax: +82 31 206 2820

Forest-like ZnO hierarchical structures were synthesized on the conductive fabric substrate via a simple one-step electrochemical deposition process. By applying externally a high cathodic voltage to the samples, ZnO microrods were aligned on the seed coated layer and then ZnO branches were formed on the pillars of ZnO microrods, which was caused by the strong deposition potential between the pillars of ZnO microrods and the $Zn^{2+}$ dissolved in growth solution. At the external cathodic voltage of –3 V, the optimized forest-like ZnO hierarchical structures exhibited high density, high porosity, and good crystallinity. These fabricated forest-like ZnO hierarchical structures are potentially useful for electronic and chemical sensing applications.



**1 Introduction** Various ZnO nanostructures, such as the nanowires, nanotubes, nanorods, nanoflowers, and hollow-urchin shaped structures, have exhibited unique optical and electrical properties, which offers considerable potential for improving the device efficiency in various application fields including piezoelectric, field emission, gas detecting, and photovoltaic devices [1, 2]. Owing to their good functionalities, hence, there has been great interest in developing porous high-density hierarchical ZnO building blocks and architectures over the past decade because they provide a largely increased surface-to-volume ratio in the integrated and combined one-dimensional (1D) ZnO nanostructures [3]. Recently, much effort has been expended to fabricate and facilitate the sea urchin or forest inspired hierarchical ZnO architectures for specific applications. Accordingly, many growth and synthesis strategies have been proposed for approaching such ZnO hierarchical architectures [4–6]. For example, Lao et al. prepared the highly ordered hierarchical ZnO nanostructure by using a vapor transport and condensation process [5]. Unfortunately, this has the disadvantage of high processing temperatures above 950 °C. Alternatively, solution-based methods have been demonstrated for low temperature and cost effective fabrication by utilizing two processing routes to grow primary and branched structures via the 3D templates such as the monolayer of microspheres and the parabolic patterned substrates [7, 8]. However, it was also somewhat complicated in preparing the primary structures or templates and subsequently organizing the 1D ZnO nanostructure building blocks. In this work, we fabricated and analyzed the forest-like ZnO hierarchical structures on conductive fabric substrates by a simple one-step process. For the synthesis, the electrochemical deposition (ED) method was used because the ZnO nanostructures can be efficiently grown on the seed coated conductive film at low temperature due to the help of applied deposition voltage.

**2 Experimental** The forest-like ZnO hierarchical structures were synthesized on conductive fabric substrates by using the one-step ED process. Herein, a commercial conductive fabric consisting of Cu-coated polyethylene terephthalate (PET) fibers with a diameter of ~20 μm was employed. For the growth substrate, the conductive fabric of 3 × 3 $cm^2$ was cleaned by ethanol and de-ionized (DI) water under ultrasonication. After dissolving 10 mM of zinc acetate dihydrate in 50 ml of ethanol, the transparent seed solution was obtained by adding the 1 ml of sodium dodecyl sulphate and stirring the solution. Then, the fabric


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substrate was immersed into the seed solution and carefully pulled up. To ensure adhesion between the ZnO seed and substrate, the sample was dried in oven at 130 °C for 3 h. As a result, the seed nanoparticles with a mean diameter of ~19 nm were uniformly coated and they acted as good nucleus sites for growing the ZnO nanorods (see Supporting Information S1 and S2, online at www.pss-rapid.com). Meanwhile, the growth solution was prepared by mixing 10 mM of zinc nitrate hexahydrate and 10 mM of hexa-methylenetetramine in 900 ml of DI water at 83–85 °C. The ED process was carried out by using the simple two-electrode system with platinum mesh. When the cathodic voltages of –2, –3, and –4 V were externally applied between the seed coated substrate and platinum mesh for 3 h, the aqueous solution was slowly stirred and kept at 83–85 °C on hotplate. During the electrochemical deposition, the current densities were approximately 0.43–0.55, 9.25–10.4, and 25.4–27.96 mA/cm$^2$ at the external cathodic voltages of –2, –3, and –4 V, respectively (as shown in Supporting Information S3). After finishing the ED process, the sample was rinsed by flowing DI water and dried in oven at 60 °C for 30 min. For investigation of morphology and structure of the fabricated forest-like ZnO hierarchical structures, a field-emission scanning electron microscope (FE-SEM, Carl Zeiss, LEO SUPRA 55) and transmission electron microscope (TEM, JEOL, JEM 200CX) were used. The growth property and crystallinity were analyzed by using X-ray diffraction (XRD, Mac Science, M18XHF-SRA).

**3 Results and discussion** Figure 1 shows (a) the schematic diagram of ZnO hierarchical structures on conductive fabric substrate and (b) a perspective view of the FE-SEM image of forest-like ZnO hierarchical structures synthesized at an external cathodic voltage of –3 V for 3 h; (c) and (d) are magnified views of FE-SEM images of the ZnO hierarchical structures. As depicted in the schematic diagram, the ZnO hierarchical structures could be densely aligned and distributed on the conductive fabric by performing the simple ED process with a high external cathodic voltage. In the perspective view of Fig. 1(b), the ZnO hierarchical structures look like a natural dense forest (compare the photographic image in the inset), sufficiently providing a large surface area. As shown in Fig. 1(c), it could be clearly observed that ZnO was formed as a complex branched architecture with primary micro-pillars (width of ~2 μm) and tremendous amount of nano-branches (width of ~100–800 nm). For a limb part of tree structure (Fig. 1(d)), many nano-branches were also hierarchically organized. After separating ZnO from the conductive fiber via the agitation and untrasonication, the TEM images and selected area electron diffraction (SAED) patterns of the detached part of ZnO were obtained as shown in Fig. 1(e). The inset shows that many ZnO nanorods were closely assembled along with the branches. From the SAED patterns at edge and joint part of ZnO branch, it was confirmed that the ZnO was grown by spontaneous crystallization from the solution into wurtzite structure at both parts.

In order to investigate the time-dependent growth behavior of the ZnO hierarchical structures in the ED process, ZnO was synthesized at different growth times of (a) 30 min, (b) 1 h and (c) 2 h under an external cathodic voltage of –3 V as shown in Fig. 2. For 30 min of the synthesis, the ZnO nanorods were vertically aligned on the seed layer with small sizes of ~30–80 nm. After 1 h, the cone-shaped ZnO microrods were formed and grown with partially originated branches. When ZnO was synthesized for 2 h, it became tree-like in structure with increased sizes of pillars and branches because the strong deposition potential enhanced the diffusion of $Zn^{2+}$ dissolved in the growth solution into the pillars of the ZnO microrods [9]. Then, the ZnO branches could be oriented at the pillar of ZnO mi-

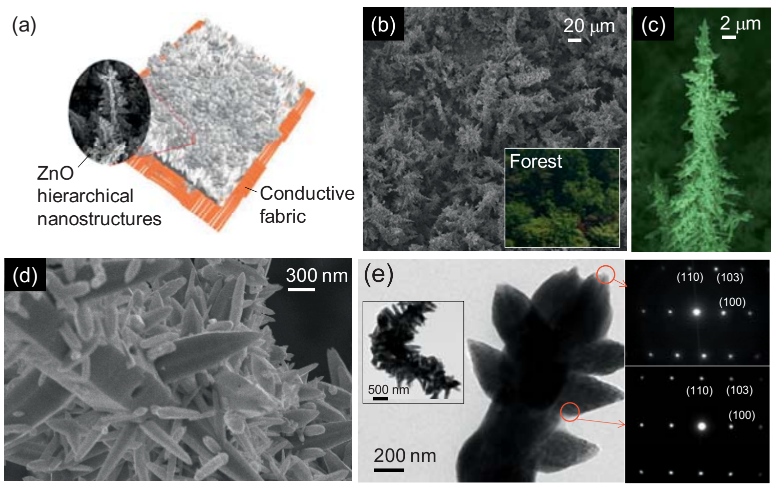


**Figure 1** (online colour at: www.pss-rapid.com) (a) Schematic diagram of the ZnO hierarchical structures on the conductive fabric substrate. (b) Perspective view of FE-SEM image of the forest-like ZnO hierarchical structures synthesized at an external cathodic voltage of –3 V for 3 h, (c) and (d) magnified view of FE-SEM images of the ZnO hierarchical structures. (e) TEM images and SAED patterns of the ZnO hierarchical structures.

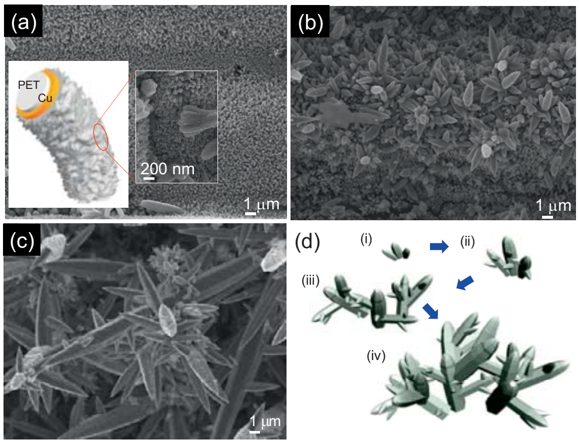


**Figure 2** (online colour at: www.pss-rapid.com) FE-SEM images of the ZnO hierarchical structures on conductive fabric synthesized at different growth times of (a) 30 min, (b) 1 h and (c) 2 h. (d) Schematic diagram of the growth mechanism.

crorods. Additionally, the ZnO nanorods were aligned again and grown at the branches. Therefore, the forest-like ZnO hierarchical structures were formed by subsequent creation and growth of branches as illustrated in Fig. 2(d).

Figure 3 shows the FE-SEM images of the ZnO structures synthesized with the relatively low and high external cathodic voltages of (a) –2 V and (b) –4 V, respectively. At –2 V, the typical morphology of ZnO nanorod arrays was also observed on the seed coated conductive fabric. At –4 V, however, the cone-shaped ZnO microrods were covered by the branches, i.e., ZnO nanorods or particles. This can be explained by the fact that high external cathodic voltage extremely increases the size of branches and attracts the already formed ZnO nanorods and particles in growth solution. The thicknesses of the fabricated samples were roughly estimated (see Supporting Information S4). Figure 3(c) shows the XRD patterns of ZnO synthesized at three different external cathodic voltages of –2, –3 and –4 V. For comparison, the XRD pattern of the coductive fabric (Cu coated PET, i.e., Cu/PET) is also shown. The bare conductive fabric exhibits the peaks of Cu and PET. For ZnO synthesized at –2 V, the dominant peak of (002) plane was observed at 34.2°. This means that the ZnO was mainly grown along the *c*-axis in wurzite structure, thus leading to the formation of the ZnO nanorod arrays. When the ZnO was synthesized at –3 V of external cathodic voltage, all XRD peaks of ZnO were largley enhanced. Particularly, the peak of (101) plane was significantly increased, which was related with the growth direction of branches. When the branches were created and synthesized on the pillar of ZnO microrods, they were grown along the diagonal direction. At –4 V of external cathodic voltage, however, the peak of (002) plane was somewhat decreased, so it was smaller than that of (101) plane. Therefore, the forest-like ZnO hierarchical structure with high crystallinity could be fabricated at –3 V of external cathodic voltage as an optimum value.

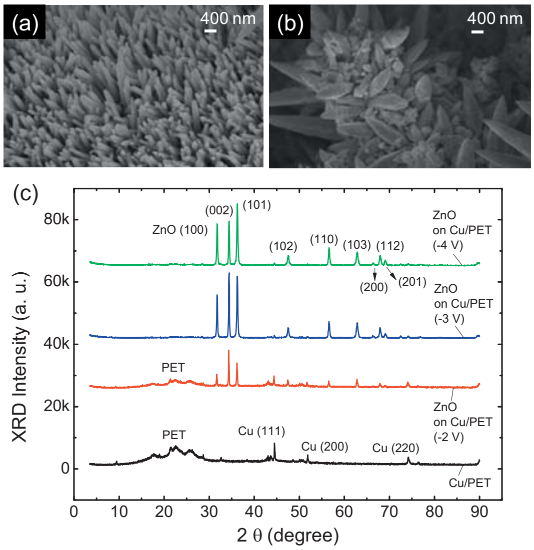


**Figure 3** (online colour at: www.pss-rapid.com) FE-SEM images of the ZnO structures on conductive fabric synthesized at different external cathodic voltages of (a) –2 V and (b) –4 V for 3 h. (c) XRD patterns for the conductive fabric and the three synthesized samples.

**4 Conclusion** We facilely synthesized forest-like ZnO hierarchical structures on conductive fabric via the one-step ED process. At an optimum external cathodic voltage of –3 V, the deposition potential assisted the creation and subsequent growth of the ZnO branches on the pillar of primary ZnO microrods. From the analysis of time-dependent growth behaviour, such subsequent synthesis and growth mechanism could be understood. Furthermore, the XRD intensity of ZnO peaks was significantly enhanced, compared to the ZnO nanorod arrays. This simple fabrication method of forest-like ZnO hierarchical structures is very promising for flexible devices as well as for ZnO based electronic and chemical sensing applications.

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