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Synthesis and Characterization of Hierarchical ZnO Micro/Nano Structures

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Abstract – Various types of hierarchical ZnO micro/nano structures have been synthesized and characterized. The tree-like hierarchical ZnO structures can grow up to 2 cm or longer. The self-organization of diverse ZnO hierarchical structures depends on the unique properties of the intrinsic polarization of the ZnO wurtzite structure, the structural symmetry of hexagonal systems and the growth kinetics. Better control over the synthesis of micro and nano hierarchical ZnO structures may provide practical applications in photonics, electronics, photovoltaics, supercapacitors, batteries, fuel cells, sensors, catalysis, and drug delivery.

Micro-structured or nano-structured hierarchical multifunctional ceramic crystals with tunable morphology may find applications in nanocomposites, photonics, electronics, photovoltaics, supercapacitors, fuel cells, sensors, catalysis, and drug delivery. Zinc oxide, with its unique physicochemical properties, has attracted intensive research interest, especially after the discovery of the ZnO nanobelts [1]. The 3D structure of the hexagonal wurtzite ZnO can be visualized by stacking along the c-axis, alternately, planes composed of tetrahedrally coordinated Zn^{2+} and O^{2-} ions, resulting in positively charged (0001)-Zn and negatively charged (0001)-O polar surfaces. Other frequently observed surfaces of ZnO crystals include the non-polar ({11-20} and {10-10}) and semi-polar ({10-1-1}, {11-22} and {10-1-3}) surfaces. The intrinsic polarity of hexagonal wurtzite crystal structure is the origin of many unique properties of ZnO. Various types of ZnO nanostructures have recently been discovered [2] and hierarchical ZnO structures have been synthesized [3]. Understanding the growth mechanisms of the self-assembled and complex hierarchical structures can provide us better control over their growth processes and help us develop complex micro or nano structures with desired properties.

The synthesis process was conducted in a mullite tube reactor with controlled flow of a mixture of nitrogen and oxygen while the growth process took place at 1050°C or lower temperatures. Hierarchical ZnO crystals grew on alumina or other types of substrates. The tree-like ZnO hierarchical structures contain many forms of micro and nano crystals and can grow as long as 2 cm or even longer. Figure 1 shows a SEM image of a small portion of a tree-like ZnO hierarchical structure, revealing the formation of aligned ZnO micro-rods grown on an interpenetrating network of ZnO micro-rods or micro-sheets. The growth direction of both the aligned micro-rods and the interpenetrating micro-rods is along the [0001] c-axis. The angles among the interpenetrating micro-rods and micro-sheets reflect the symmetry of the hexagonal structure. Figure 2 shows a SEM image of another portion of the tree-like ZnO hierarchical crystals, revealing the formation, via self-assembly, of shelf-type or box-type microstructures composing of nanoribbons or nanoneedles. The complex growth patterns of ZnO hierarchical structures are determined by the synthesis parameters. The self-assembly of diverse ZnO hierarchical structures depends on both the nature of ZnO wurtzite structure and the nucleation and growth kinetics.

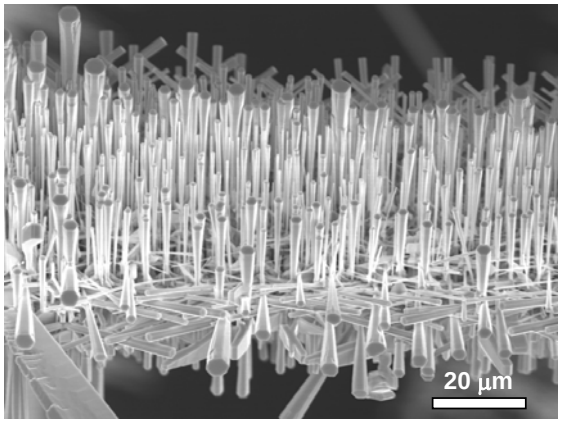

Figure 1: SEM image shows hierarchical growth of aligned and interpenetrating ZnO micro-rods.

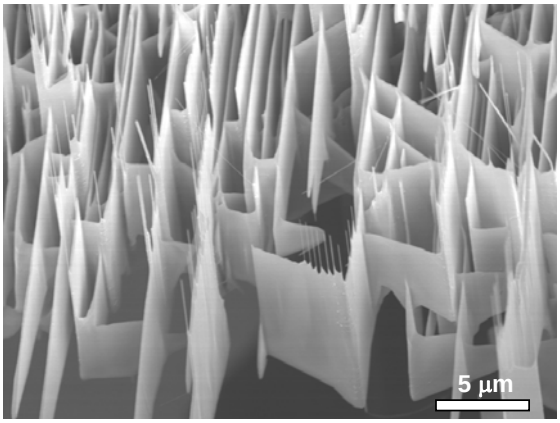

Figure 2: SEM image shows the formation of shelf-type or box-type microstructures consisting of ZnO nanoribbons.

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[2] Z. L. Wang, Materials Science & Engineering R 64 (2009) 33.
[3] J. Y. Lao, J. G. Wen, and Z. F. Ren, Nano Letters 2 (2002) 1287.