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New growth equation for ZnO rods

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We report a novel equation for the growth of ZnO rod-like structures fabricated via a catalyst-free combust-oxidised process (CFCO). The generic form of the growth equation is $\boldsymbol{\psi} = \boldsymbol{\nu}\mathbf{L} + \boldsymbol{\eta}_\mathbf{o}$ where $\boldsymbol{\psi}$ is the aspect ratio, **L** is the length of ZnO rods along ±[0001] direction, $\boldsymbol{\nu}$ is the slope of the $\boldsymbol{\psi}$-**L** graph and $\boldsymbol{\eta}_\mathbf{o}$ is the initial growth constant. Two values for the slope $\boldsymbol{\nu}$ are discovered, namely 3.75 pm^{-1} and 9.65 pm^{-1} that indicate there are two groups of rod-like structures. In CFCO process, ZnO rods grow rapidly along the polar ±[0001] direction at a fast rate exceeding 100 nm per second. The morphology of ZnO rods is examined using FESEM, TEM and XRD.

I. INTRODUCTION

High-surface-area ZnO powder (above 7.5 m^2/g) is occasionally composed of rod-like clusters, as illustrated by the FESEM micrographs in Fig. 1. The inset micrographs show typical wurtzite structure of ZnO nanorods with hexagonal cross section. From our previous work on CFCO ZnO [1,2], we have observed that hexagonal rods are the preferred morphological configuration in localized areas relatively richer in oxygen content whereby rectangular nanoplates/boxes are the preferred ones in localized regions containing relatively lower oxygen partial pressure. Due to the big diversity in growth conditions in CFCO process, rods of different lengths and widths are observed, as shown in Fig. 1, and this phenomenon allows us to investigate the salient features of their growth.

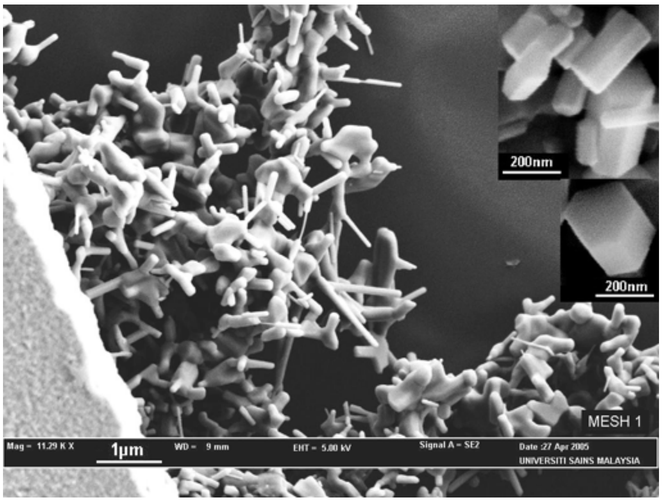

FIG. 1. FESEM micrograph of ZnO nanorod clusters, insets show quasi-hexagonal morphology.

II. EXPERIMENT

ZnO material is obtained from the industry and the specific surface area of the ZnO is 7.5 m^2/g. The ZnO powder is characterized by LEOSupra50VP field emission scanning electron microscope (FESEM), SiemensD5000 x-ray diffractometer (XRD) and PhillipsCM12 transmission electron microscope (TEM). The lengths and widths of 150 rods are determined by measuring directly from TEM and FESEM micrographs.

III. RESULTS AND DISCUSSIONS

FESEM and TEM micrographs in Fig. 2 show ZnO rods with different lengths and various aspect ratios; and interestingly enough, these diverse rods coexist and co-diffuse in clusters even in a minute region of 1 μm^3 giving rise to the condition of *nanoscopic inhomogeneity* The morphological diversity also indicates differences in the growth conditions such as growth time, temperature and oxygen-to-zinc partial pressure ratio. The XRD data and selected area electron diffraction (SAED) pattern, taken from one of the hexagonal heads of the rods, confirm the polycrystalline nature of ZnO rods as indicated by the ring pattern referring to diffraction peaks at 56.5º $(11\bar{2}0)$, 68.2º $(11\bar{2}2)$, 76.2º $(20\bar{2}2)$ and 81.8º $(10\bar{1}1)$, as posted in Fig. 2(e).

In determining the aspect ratio, there exists a measurement error [3] in the width dimension whereby the smallest width is obtained if the FESEM/TEM micrograph is perpendicular to the $[2\bar{1}\bar{1}0]$ direction whilst the largest width refers to the $[10\bar{1}0]$ direction, as illustrated in Figs. 3(a) and 3(b). Using Miller-Bravais coordinate system, the maximum error is about 14% based on a perfect hexagon. About a quarter of ZnO rods possess tapered cross section along the longitudinal c-axis ([0001]), and the average width is obtained by averaging the middle and end widths (Fig. 3(c)). Based