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Hydrothermal growth of 3 dimensional porous ZnO nanoflowers and functional properties

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1. Introduction

Zinc oxide (ZnO) is a wide band gap (3.37 eV) II-VI semiconductor with extensive applications such as room temperature lasing, optoelectronics, photocatalysis and sensors. Over the past decades, tremendous attempts have been made to synthesize various ZnO nanostructures such as nanoparticles, nanobelts, nanosheets, nanowires, nanoflowers etc. Various methods have been devoted to synthesize the ZnO nanostructures such as vapour phase transport, chemical vapour deposition, spray pyrolysis deposition, microwave assisted chemical route, hydrothermal, solvothermal method and wet chemical method. Hydrothermal method has realized a feasible route to fabricate micro and nano ZnO building blocks with variety of nano architectures. Recently, several research works have been reported on the hydrothermal growth of ZnO nanostructures [1,2]. For example, Benxia Li and Yanfen Wang synthesized flower-like ZnO hierarchical microstructures with enhanced photocatalytic activity by low temperature aqueous solution method. Genki Saito et al reported the plasma assisted solution synthesis of ZnO nanoflowers. Anlian Pan et al demonstrated the hydrothermal growth of ZnO nanoflowers made from ZnO nanosheets. Seung-Ho Jung et al prepared variety of ZnO nanostructures including nanoflower morphology by sonochemical method. However, the growth mechanisms of 3 dimensional nanostructures by solution methods are assumed as an oriented attachment growth under hydrothermal ambient conditions. Moreover, there is no report for the evidence of such a growth behavior of nanostructures. In the present work, we report the formation mechanism of 3 dimensional ZnO nanoflowers from 1 dimensional nanorod under hydrothermal growth conditions and experimentally evidenced the oriented attachment growth of nanostructures. The hydrothermally grown ZnO nanostructures have been characterized by X-ray diffraction pattern (XRD), Field emission scanning electron microscope (FESEM), transmission electron microscope (TEM) and photoluminescence spectrophotometer.

2. Experimental procedure

All the chemicals were purchased from WAKO chemicals Japan with analytical grade purity. A typical experimental procedure is as follows: 0.2 M of zinc acetate and 0.2 M of sodium hydroxide were dissolved in 50 mL of de-ionized water under magnetic stirring at room temperature. 0.05 M of triethylamine was added drop wise to the reactant solution. The reaction process was continued for 10 h under vigorous stirring at 460 rpm. After that the solution was transferred to the Teflon lined 100 mL capacity autoclave, to which ultrasonically cleaned fluorine doped tin oxide (FTO) substrate was placed at the bottom of the PTFE crucible. The autoclave was tightly sealed and it was kept in a furnace for hydrothermal growth. The temperature of the furnace was increased to 200 ˚C and the growth period was maintained up to 15 h. After the hydrothermal growth, the autoclave was allowed to cool to room temperature and then the FTO substrate was taken from the solution. ZnO nanostructures deposited FTO substrate was initially dried at 90 ˚C on a hot plate for 30 minutes and subsequently annealed at 200 ˚C for 1 h in a furnace. In a similar manner, the hydrothermal growth period was changed to 25, 40 and 48 h.

3. Results and discussions

Fig. 1 (a) shows the FESEM image of 15 h grown ZnO nanostructures on FTO substrate. ZnO nanostructures resembled nanorods and the monodispersity in size and morphology was seen. Figs. 1 (b) and (c) show the TEM images of nanorods. The diameter of an individual nanorod was 130 nm and the length was 450 nm. Bottom view of an individual nanorod was visualized by TEM as shown in Fig. 1 (d) and exhibit the hexagonal morphology. Based on the morphological observation by TEM, a growth mechanism is proposed as shown in Fig. 2. The nanorods were grown with the diameter of 110 nm and size of 450 nm at the initial stage. The secondary growth began on the side wall up to 20 nm from the bottom of the nanorods as marked in the Fig. 2. (c) by the arrows. However the secondary growth did not continue upto the full length of nanorods (450 nm) and completed about 250 nm. This may be due the lack of Zn and OH adatoms in the solution. This growth behavior occurred in the entire sample. The size of primary grown part of nanorods and secondary grown area were highly monodispersed in the sample. HRTEM images showed clearly the lattice fringes which indicated that the ZnO nanorod was in crystalline nature. In addition to that the triethylamine molecules acted as surface passivating ligand and thus restricted the agglomerations and initialized the growth along a particular plane [3].

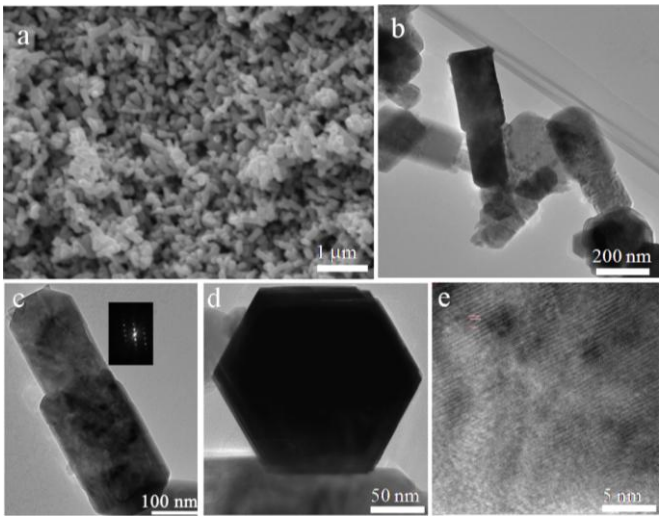

Fig. 1. (a) FESEM, (b-d) TEM and (e) HRTEM images of 15 h grown ZnO nanorods.

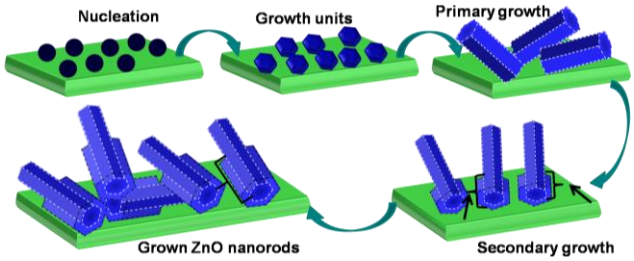

Fig.2. Growth mechanism of ZnO nanorods for 15 h growth.

Fig. 3 (a) shows the FESEM image of the sample grown for 25 h on FTO substrate. It showed the distribution of ZnO nanorods with monodispersity. However, some of the places (white circle marked) had ball-like nanostructures with the diameter of 8 μm. Fig . 3 (b) shows the magnified marked region of ZnO nanostructures. The morphology of nanostructure resembles a ball-like three dimensional architecture. Moreover, the ball-like nanostructure consisted of ZnO nanorods. as shown in Fig. 3(c).

In the hydrothermal growth process, the nucleation and growth depend on the growth temperature and the pressure inside the autoclave. Figs. 4 (a), (b) and (c) show the FESEM images of ZnO nanostructures grown for 40 h. The ball-like ZnO nanostructures were transformed to sheet-like morphology due to the oriented attachment growth behavior for longer growth time of 40 h. Whereas Figs. 4 (d), (e) and (f) show the FESEM images of ZnO nanostructures grown for 48 h. The porous 3 dimensional flower-like morphology was seen. This growth was observed in the entire substrate with monodispersity in size and morphology.

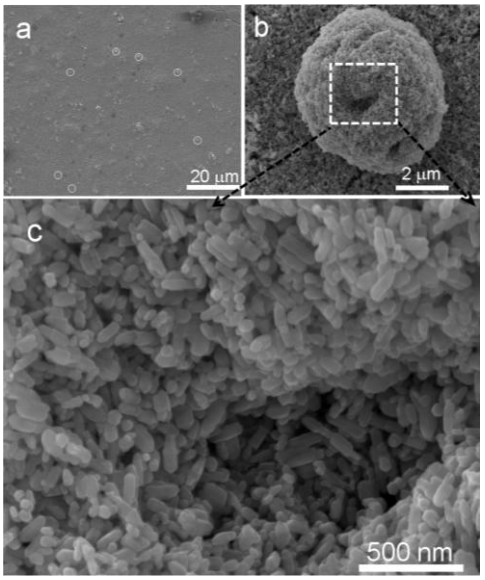

Fig. 3. (a), (b) and (c) FESEM images of 25 h grown ZnO nanostructures.

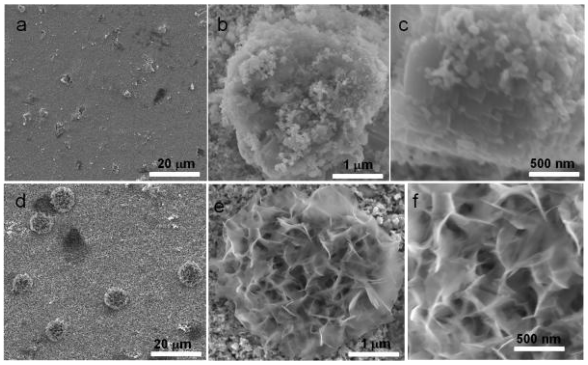

Fig.4. (a), (b) and (c) FESEM images of 40 h grown ZnO nanostructures, (d), (e) and (f) FESEM images of 48 h grown ZnO nanostructures,

4. Conclusion

The change of growth behavior of ZnO nanorods to 3 dimensional porous ZnO flower was observed by hydrothermal growth. Triethylamine molecules effectively facilitated the monodispersed ZnO nanorods for the 15 h growth. The higher growth time of 40 and 48 h and high temperature of 200 ˚C yielded the 3 dimensional morphology of ZnO.

References

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