



Two-dimensional crystal growth in ZnO nanostructures directed by poly vinylpyrrolidone

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ABSTRACT

Zinc oxide nanostructure favors to grow along with the c-axis and adopt the stable hexagonal wurtzite phase so that the crystal growth produces hexagonal-shaped nanorods or nanoplates. In this work, we demonstrated that the crystal growth preference in the c-axis direction in ZnO nanostructure can be modified to produce an ultimate two-dimensional nanostructure by polyvinylpyrrolidone (PVP) surfactant under an alkaline condition of hydrothermal reaction. We found that the nanosheet dimension depends on the concentration of NaOH. The ultrathin nanosheet of ZnO should find used as active material in optoelectronic device applications.

1. Introduction

The two-dimensional (2D) nanostructure of semiconducting materials are highly demanded due to its unique optical and electrical properties, the result of ultimate two-dimensional carrier confinement [1]. ZnO nanostructures have been widely explored for morphology modification due to their high-exciton binding energy, highly reactive surface the result of unique zinc and oxygen terminated surface, and high-electron mobility [2]. This places the ZnO nanostructure as potential materials in photocatalysis [3], solar cells [4], and surface biological activity [5]. The preparation of ZnO nanostructures in the form of ultimate thin 2D structure should enhance the existing properties due to its high-density surface atom and 2D carrier dynamic. Unfortunately, there has been a scarce effort to prepare the ZnO nanostructures in the form of ultra-thin nanosheets due to limited techniques to control the crystal plane growth preference.

Here, we present a preliminary but highly effective method to promote 2D crystal growth in ZnO nanostructure, producing an ultimate-thin nanosheet directly on the substrate surface. The nanosheet's growth depends on the PVP surfactant and is sensitive to the concentration of NaOH in the reaction. The nanosheet dimension is enlarged with the increase of NaOH concentration. The nanosheet's thickness is

estimated to be 5 nm. The 2D nanostructure of ZnO should find extensive use as an electron transport layer of perovskite solar cells, photocatalyst, and sensors.

2. Experimental

Ultra-thin ZnO nanosheets were prepared using a hydrothermal method at 90 °C. In the typical procedure, a growth solution containing 0.05 M of zinc nitrate hydrate, Zn(NO₃)₆H₂O (Alfa Aesar), 1 mg/mL of polyvinylpyrrolidone (PVP) (Sigma-Aldrich, USA), and 1 mL of 1 M NaOH (WAKO Chemical, Japan). A pre-cleaned FTO substrate that was prepared by ultrasonication in acetone and ethanol each for 15 min was then immersed vertically into the reaction. The reaction container was air-tight capped and transferred into a pre-heated electrical oven for a hydrothermal reaction at 90 °C. The growth reaction was performed for 2 h. The sample was then washed with pure water dried with a nitrogen gas flow, and heated on a hot plate at 250 °C for 1 h.

The morphology and the phase crystallinity of the samples were analyzed using a field emission scanning electron microscopy (FESEM) Zeiss Supra 55VP and X-ray diffraction (XRD) measurements using Bruker D8 Advance with CuK α radiation ($\lambda = 1.541 \text{ \AA}$) and a scan rate of 2°/min, respectively.

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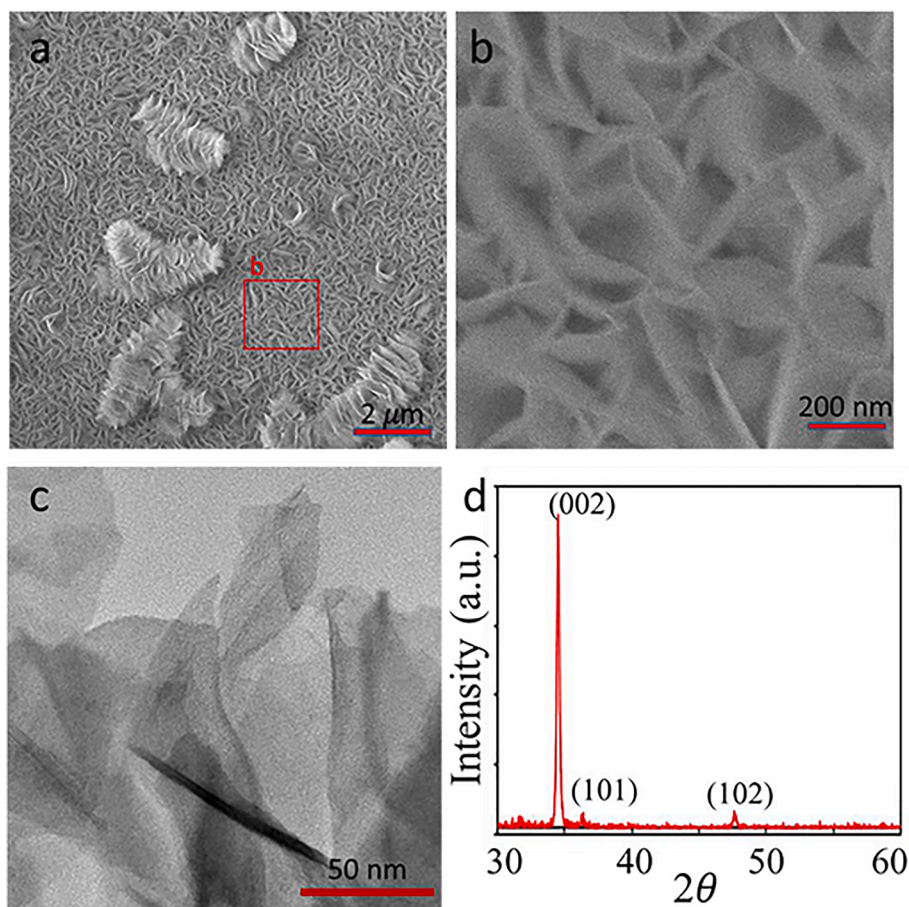


Fig. 1. (a and b) Low and high-resolution FESEM images of ZnO nanosheets on FTO substrate. (c) low-resolution TEM image. (d) X-ray diffraction pattern of the sample.

3. Results and discussion

Fig. 1 shows the typical 2D structure of ZnO grown on an FTO substrate. The sample was prepared using a 10 mL growth solution containing 0.05 M zinc acetate hydrate, 1 mg/mL PVP, and 1 mL of 1.0 M NaOH. The growth temperature was 90 °C. As Fig. 1a shows, the ZnO nanosheet has effectively grown on the substrate's surface. The nanosheet is vertically oriented (Fig. 1b) instead of the planar structure. From Fig. 1b, we also can see that the nanosheet collides with each other,

producing a nanosheet network structure. This provides a large surface area. The nanosheets' thickness is estimated to be approximately 5 nm. The nanosheets' vertical length cannot be obtained due to limited techniques for cross-section analysis. From Fig. 1a, a cluster of nanosheets are seen to form on top of vertical oriented nanosheet. The cluster comes from the bulk solution that drops onto the surface during the growth process. It can be removed by a proper ultrasonication before post-growth annealing process. Fig. 1c shows a low-resolution transmission electron microscopy (TEM) image of the sample. The result

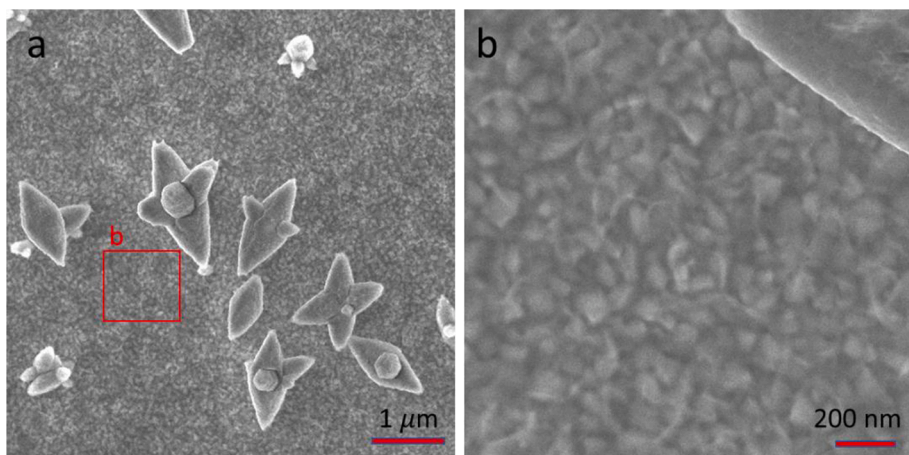


Fig. 2. ZnO nanostructure growth under the lower concentration of NaOH, i.e. 1 mL of 0.1 M. (a) low and (b) high magnification image taken at the specified area in a. Large flower-like structures are ZnO crystals that grow in the bulk solution and then drop onto the surface during the growth process.

indicates that the nanosheet is crystalline solid and is not a porous structure.

We verified the nanosheet's phase crystallinity using X-ray diffraction analysis. The result is shown in Fig. 1d. As presented in Fig. 1c, the XRD pattern contains one strong peak at 2θ 34.5° and two weak peaks at 36° and 47.5° . We found that the XRD pattern matches well with the JCPDS File no. 36-1451 for hexagonal wurtzite phase of ZnO with peaks at 34.5° , 36° , and 47.5° are associated with the diffraction from (002), (101) and (102) Bragg planes, respectively. From the XRD pattern, we can see that the diffraction from the (002) plane is very strong and incomparable to the other two peaks. This indicates that the nanosheet is characterized by the dominant (002) plane, which is amongst the highest energy facet of wurtzite ZnO. This feature is demanded in photocatalysis and optoelectronics devices applications.

The growth of ZnO nanosheet on the substrate surface is solely due to the effective two-dimensional crystal growth by the PVP surfactant under alkaline conditions. ZnO nanostructure growth in most wet chemical preparation approaches produces irregular shape nanoparticles [6] and in the presence of surfactant or directing agent realized nanorods morphology [7]. Vertical oriented nanosheet has been previously realized on the substrate surface in the presence of Al catalyst. To our best knowledge, the present approach is the first technique for growing vertical oriented ZnO nanosheet directly on the substrate surface, promoted by surfactant's two-dimensional directed growth. PVP has been reported to be effective in realizing 2D crystal growth in Au nanostructure [8] and in combination with other surfactants, such as cetyltrimethylammonium bromide, can realize highly thin Au nanoplates on the surface. 2D crystal growth in ZnO nanostructure is assumed to follow a similar mechanism as presented in Au nanoplates formation [8], i.e. efficient passivation of (001) plane of the wurtzite phase by the carbonyl ligand in the polymer backbone via -O-Zn coordination. This coordination is strong as no by-product produces from the reaction. A detailed discussion of the growth mechanism is given in the [Supplementary File](#).

The 2D crystal growth is sensitive to the concentration of NaOH in the reaction. For example, when the concentration of NaOH decreases, the dimension (vertical length and the thickness) also decreases. Fig. 2 shows the ZnO nanosheets prepared under NaOH concentration decrease to ten times from the one in Fig. 1. It is found that although the physical dimension of the nanosheet decrease the nanosheet effectively covers the substrate surface. From the image, large flower-like crystals are also observed. These are the ZnO's crystallite that grows in the bulk solution and drops onto the surface of the substrate during the reaction. They can be removed by proper ultrasonication to produce a clean ZnO nanosheet on the surface. This sample is prepared with PVP concentration similar to the one in Fig. 1. The formation of large flower-like crystallite in the bulk solution indicates that the low concentration NaOH does not effectively activate the passivation ability of the PVP on the growing plane of the ZnO nanocrystals. Thus, we remark that a synergetic combination effect of PVP and NaOH is required for a large-scale 2D crystal growth of ZnO.

To rule out the post-growth annealing effect on the nanosheet growth, we evaluated the as-prepared sample's morphology. The result indicated that the nanosheet morphology is similar to the one after being annealed ([Supplementary File](#)), confirming the 2D crystal growth occurred in the growth solution.

This result is still preliminary, reporting the special function of PVP in promoting vertical 2D crystal growth in ZnO nanostructure, which is not available in other surfactant systems. The use of the combinative effect of PVP, urea, NaOH under relatively higher reaction temperature has also been reported in the synthesis of ZnO nanostructures [9–11]. However, they only yielded micro-sized hierarchical nanoplates. Free-standing nanoplates or thin nanosheet was not projected from these approaches. It is in stark contrast to our present result where we achieve fine control over kinetic growth of ZnO nanostructure via the synergized combinative effect of PVP and NaOH, realizing vertical 2D crystal

growth on the surface. Further detailed analysis should indeed be conducted to show the dynamic of 2D crystal growth under the different combinative effects of NaOH and PVP. This is under our current study and will be reported in different communication.

4. Conclusions

We conclude that the 2D crystal growth in ZnO nanostructure is achieved via the synergetic effect of PVP surfactant and NaOH. The 2D nanosheet covers effectively the substrate surface without the existence of the void, which is potential for optoelectronic device application, such as solar cells and light-emitting diode. The thickness of the nanosheet can be controlled by the concentration of NaOH that opens the possibility to harness the quantum effect generated from the ultimate 2D carrier confinement in ZnO for performance's improvement.

CRedit authorship contribution statement

Marjoni Imamora Ali Umar: Resources, Investigation, Formal analysis, Data curation, Writing – original draft. **Dahyunir Dahlan:** Resources, Investigation, Formal analysis. **Muhammad Nurdin:** Formal analysis, Investigation. **Munetaka Oyama:** Formal analysis, Investigation. **Akraj Ali Umar:** Conceptualization, Supervision, Methodology, Validation, Writing – review & editing, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.matlet.2021.130649>.

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