Supplementary Material (ESI)

Optimized model structures

We constructed the periodical supercell model by setting the slab thickness, terrace width and distance between edges, as shown in Fig. S1(a). To find optimized model resulting in the most accurate results, we adjusted the parameters of slab thickness, terrace width and distance between edges. According to Fig. S1(b), distance of 4 unit cells length between edges could attain a stable value for 4 cells terrace width. Then, we fixed 4 cells distance and tested the influence of terrace width. From Fig. S1(c), we found the size of 10 or 12 cells length was available due to the difference of 0.004 eV for the two values. Considering the small value of terrace width when testing the distance between edges, we chose distance of 6 cells and terrace width of 10 cells for following calculations. For the step structures on (0001)-Zn surface, the optimized slab was of 4 single layers thickness with bottom layer passivated by hydrogen, which could be seen from Fig. S1(d) and (e). Nevertheless, 4 layers thick slab without hydrogenation of bottom layer could be chosen for simulation on (000$\bar{1}$)-O surface according to our form work (CrystEngComm, 2012, 14, 355).

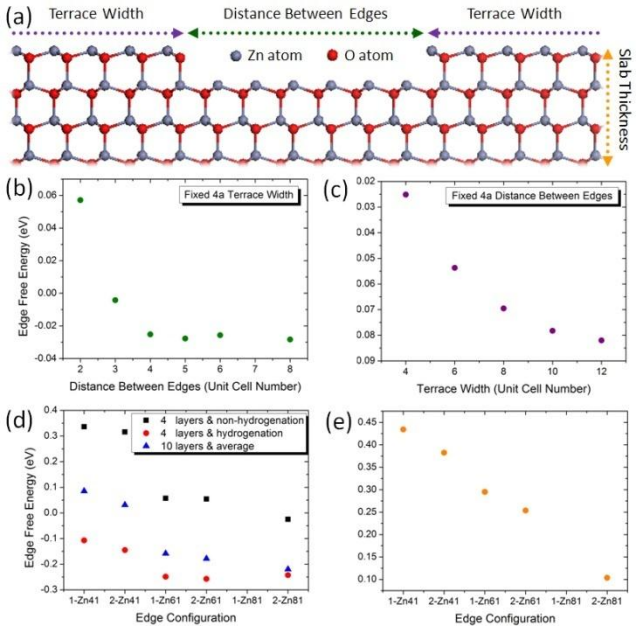

Fig. S1 Periodical supercell model with the illustrations of the slab thickness, terrace width and distance between edges. (b) and (c) Structural test of the distance between edges and terrace width for DFT calculations, respectively. (d) The effect of hydrogen passivation, i.e. hydrogenation, on the bottom layer for step models on (0001)-Zn surface with the case of 10 layers slab as a reference. Results of "10 layers & average" were calculated by averaging the values with and without hydrogenation. (e) Correcting ratio is defined as: the difference between non-hydrogenating and hydrogenating 4 layers case in figure (d) divided by the difference between average 10 layers and hydrogenating 4 layers case. A linear decreasing trend indicates that for larger structures, such as the model used in our formal calculation, 4 layers slab with bottom atoms passivated by H atoms can simulate the real case well. The detailed edge configurations are shown in Fig. S2.

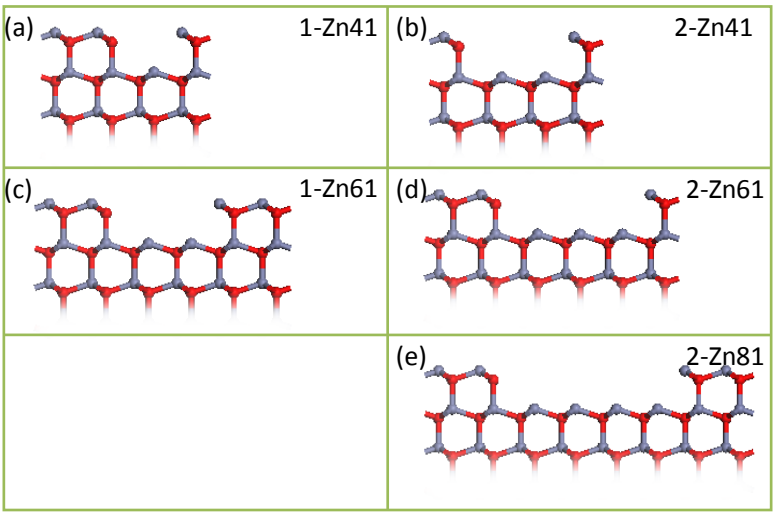

Fig. S2 Detailed edge configurations mentioned in Fig. 4(d) and (e). The terrace width and distance between edges are equal in models (b), (d) and (e). For (a) and (c), the distances are smaller.

Diameter shrinkage at a fixed temperature

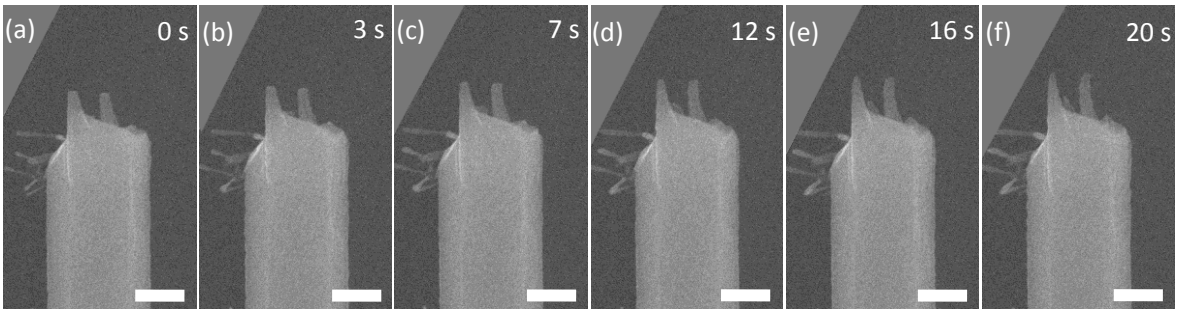

Fig. S3 *In-situ* observation of nanowire growth at a fixed temperature of 700^{o}C with time progressing. The reference time is labeled at the top right corners in (a-f). The diameter of the epitaxial nanowire shrinksin this process. Scale bar for (a-f): 1 μm.

O-terminated edges for (0001)-Zn surface

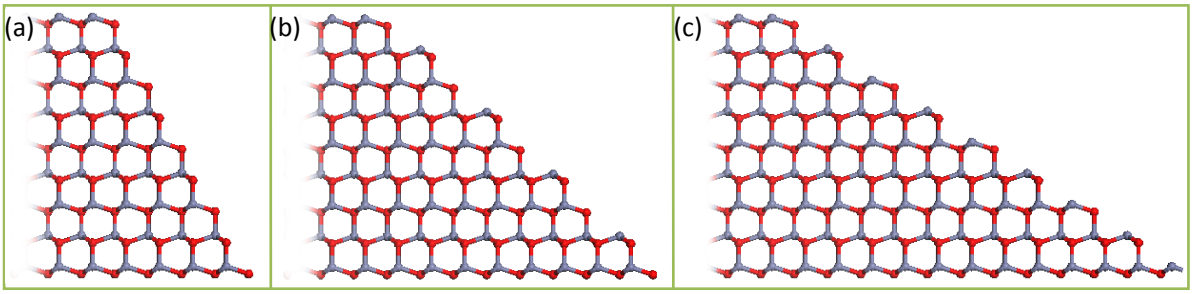

Fig. S4 The cross-sectional stable atomic structures along [11-20] orientation of hexagonal pyramid for different side face indexes on (0001)-Zn surface. O terminated edges can be found in all these structures.

Growth rate (difference) calculation

Theoretically, we can calculate the growth rate difference by a two-dimensional (2D) nucleation and multilayer growth mode. Here, we estimate the step advance rate by a simplified single step mode, which is applicative due to a large distance between two adjacent steps indicated by our experiments (inset in Fig. 3(b)) and other STM results (Surface Science 519 (2002) 201–217).

The growth rate can be written as:

$$R \cong a(J_0 v^2)^{1/3}$$

where a, J_0 and v are the lattice constant, 2D nucleation rate and step advance rate, respectively. By calculating proper parameters, we estimate growth rates for the two polar faces, and the calculated results were summarized in Fig. S5. The growth rate on Zn surface is significantly higher than on O surface.

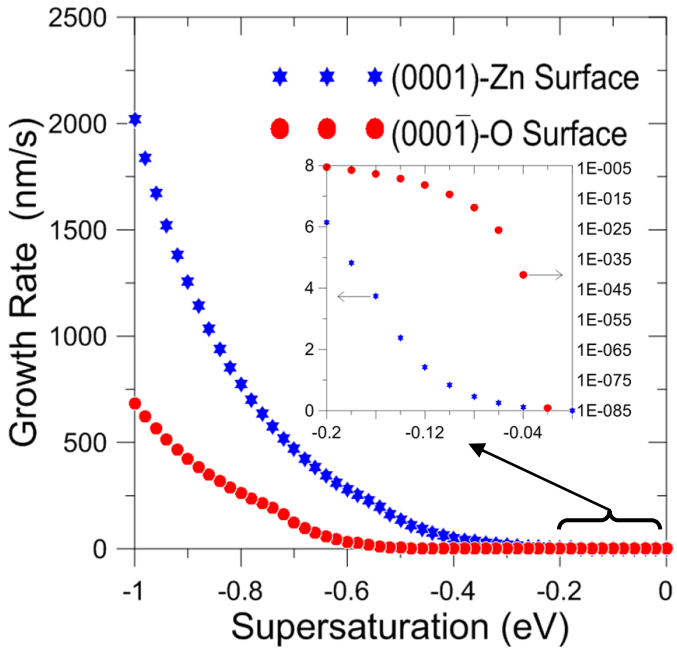

Fig. S5 Calculation results of growth rate for (0001)-Zn surface and (000-1)-O surface.