Supplementary Information

Position-controlled hydrothermal growth of ZnO nanorods on arbitrary substrates with a patterned seed layer *via* ultraviolet-assisted nanoimprint lithography

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Characterization of the as-imprinted ZnO patterns and the ZnO seed used for hydrothermal growth

XRD was used to characterize both the as-imprinted ZnO patterns and the ZnO seed, i.e. the ZnO patterns etched with Cl_2 plasma followed by annealing at 120 ^{o}C for 1 h. As shown in Figure S1a, the as-imprinted ZnO patterns consisted of amorphous ZnO while weak diffraction peaks of wurtzite ZnO were obtained from the ZnO seed. The ZnO seed was also analyzed by cross sectional TEM, and the obtained images are shown in Figure S1. The high-resolution TEM image (Figure S1c) reveals lattice fringes from small crystallites of a few nm and an amorphous background, indicating the coexistence of both amorphous and polycrystalline phases. Combining the XRD results and TEM images, we believe that the as-imprinted ZnO patterns are amorphous, but the ZnO seed contains both amorphous and polycrystalline phases at the cost of a Cl_2 plasma etch followed by annealing at 120 ^{o}C.

Quantitative analyses of ZnO nanorods resulted from different growth times and different substrates

Quantitative analyses were performed to reveal the diameter and length relationships of ZnO nanorods with the growth time. The diameters and lengths were measured from cross-sectional SEM images, as shown in the insets of Figure 3a-f. The average diameter of ZnO nanorods grown on p-Si(100) substrates, as a result of different growth times for 2, 3, 4, 5, 6 and 12 h, was found to be 40, 61, 70, 78, 86 and 130 nm, respectively and the average length was 109, 252, 397, 472, 1012 and 1263 nm, respectively. These data were plotted against the growth time as shown in Figure S2. The growth rate in length is much faster than that in diameter, as a result of preferential [002] growth in the presence of hexamethylenetetramine (HMT). In addition, for the growth time from 0 to 6 h, the diameter curve features a fast initial growth followed by a slower subsequent growth while the length curve displays an opposite.

The above observation could presumably be interpreted as the following. During the initial growth, colloidal ZnO particles formed in the growth solution are small and the shape of the ZnO nanostructures growing on the substrate is close to spherical, e.g., the aspect ratio of ZnO nanorods is

2.7 at a growth time of 2 h. The small colloidal ZnO particles could efficiently supply the growth of ZnO nanorods on all their exposed surfaces. However, as the growth proceeds, the colloidal ZnO particles in the growth solution become larger and the aspect ratio of ZnO nanorods is high (e.g., 11.8 at 6 h) owing to the HMT-assisted growth. The larger colloidal ZnO particles could not supply the growth on nanorod sidewalls as efficiently as on nanorod tips, possibly due to both the material transport limitation of colloidal particles and the spatial hindrance for radial growth. Meanwhile, the growth on nanorod tips is faster as a result of attaching larger colloidal particles at the tips during growth. With long growth times (i.e., 6 to 12 h), the precursor concentration of growth solution is continuously lowered and the nanorods from adjacent seeding ZnO patterns interfere with each other, resulting in a slowed axial growth.

The effect of different substrates on the population and length of ZnO nanorods grown for 5 h was investigated and the results are shown in Figure S3. Based on the total ZnO nanorods observed in each of the SEM images under a given magnification as shown in the Figure 5b, e and h, the average number of ZnO nanorods per micrometer for each line and the corresponding average nanorod length were determined. The average number of ZnO nanorods, obtained on p-Si(100), glass and PET substrates, was found to be 52, 61 and 59 μm^{-1}, respectively and the corresponding average length was 485, 424 and 394 nm, respectively. These results show that the substrate substances have little influence on the population and growth rate of ZnO nanorods.

Supplementary Figures

Figure S1

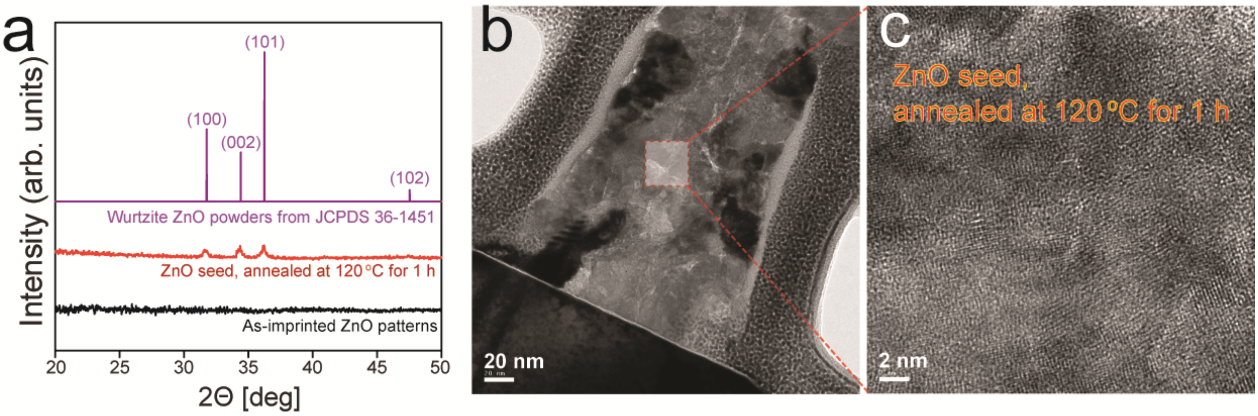

Figure S1. (a) XRD spectra of the as-imprinted ZnO patterns, the ZnO seed (i.e., the ZnO patterns etched with Cl_2 plasma followed by annealing at 120 ^{o}C for 1 h), and the standard power diffraction pattern of a wurtzite ZnO powder from JCPDS 36-14561. (b) A cross-sectional TEM image of the ZnO seed. (c) A high resolution TEM image obtained from the region highlighted by the dotted box in (b).

Figure S2

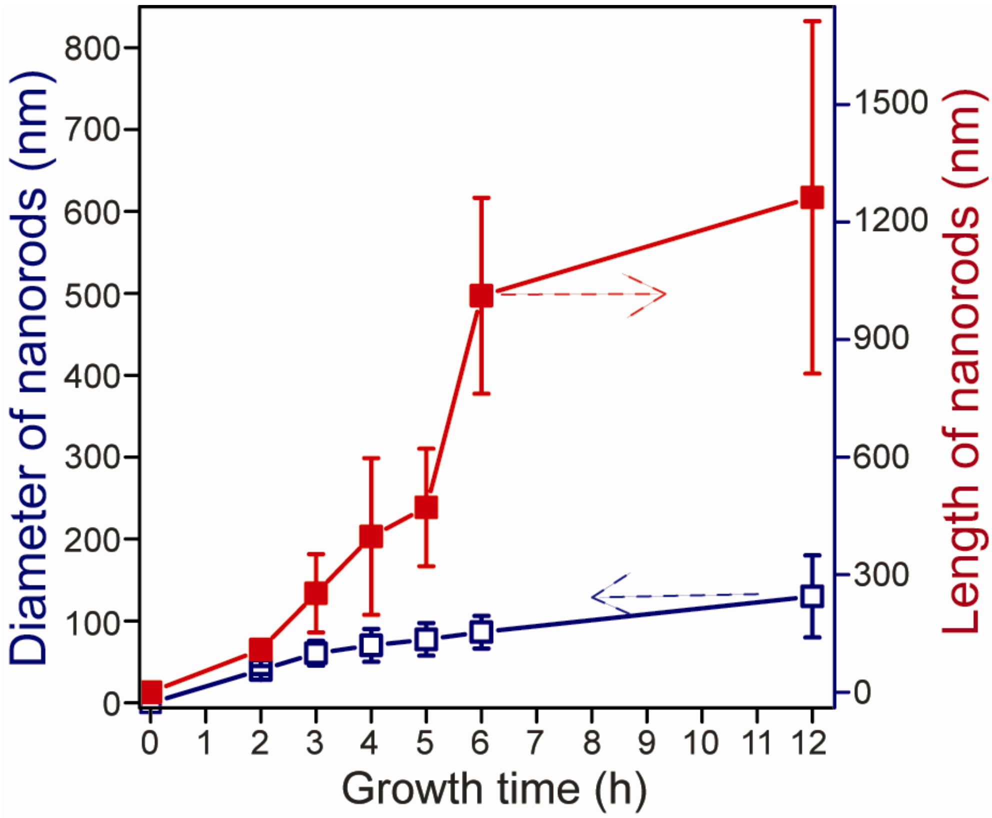

Figure S2. Dependences of ZnO nanorod diameter (the left-hand vertical axis) and length (the right-hand vertical axis) on the growth time.

Figure S3

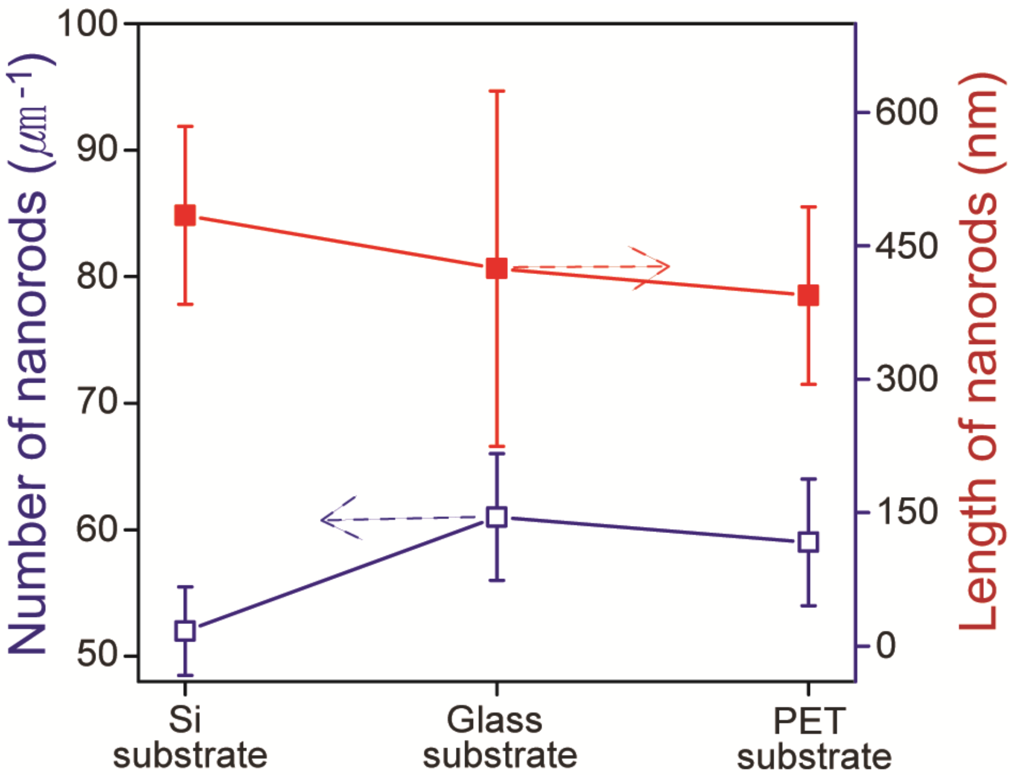

Figure S3. The population (the left-hand vertical axis) and length (the right-hand vertical axis) of ZnO nanorods grown for 5 h on different substrates.