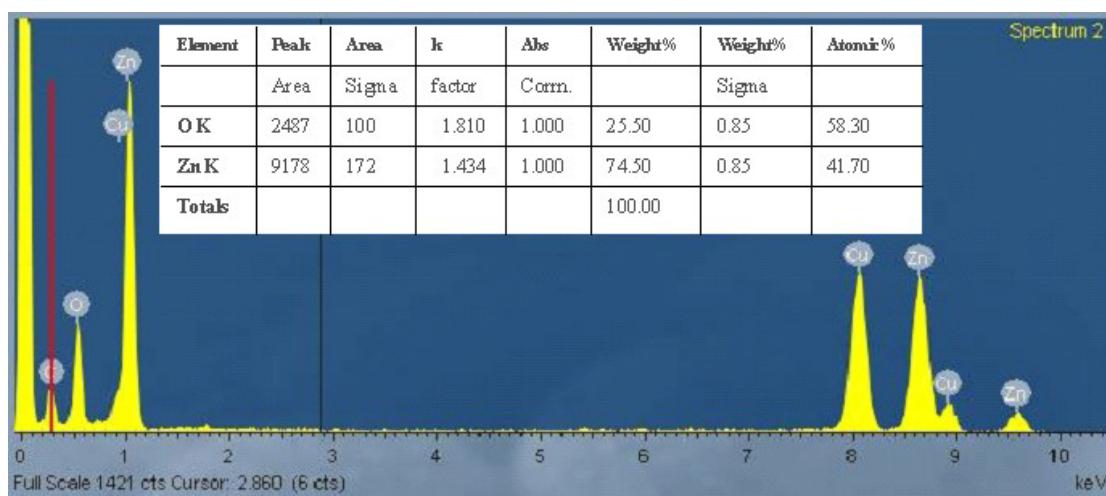


## Supporting Information

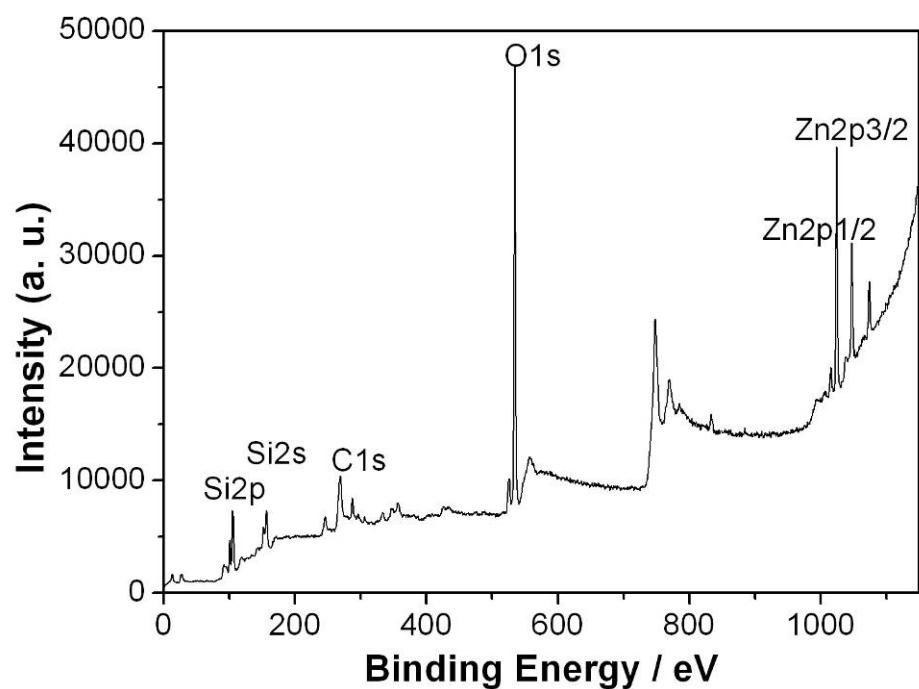
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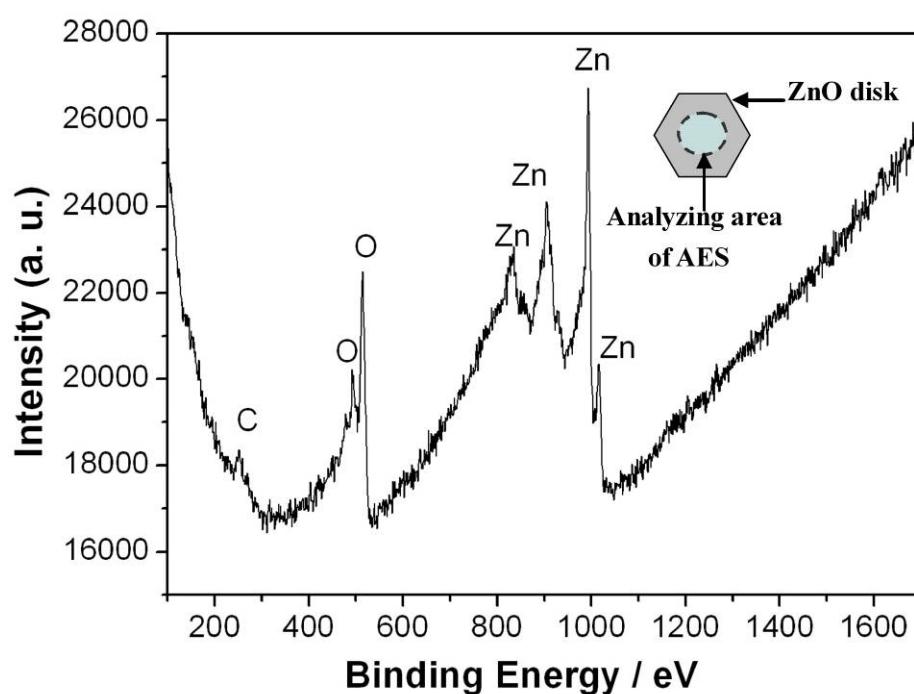
**Figure S1.** EDS spectrum of a typical nanocrystalline ZnO hexagonal disk calcinated at 500°C for 4 hours, indicating that no presence of F residue in ZnO nanostructures.



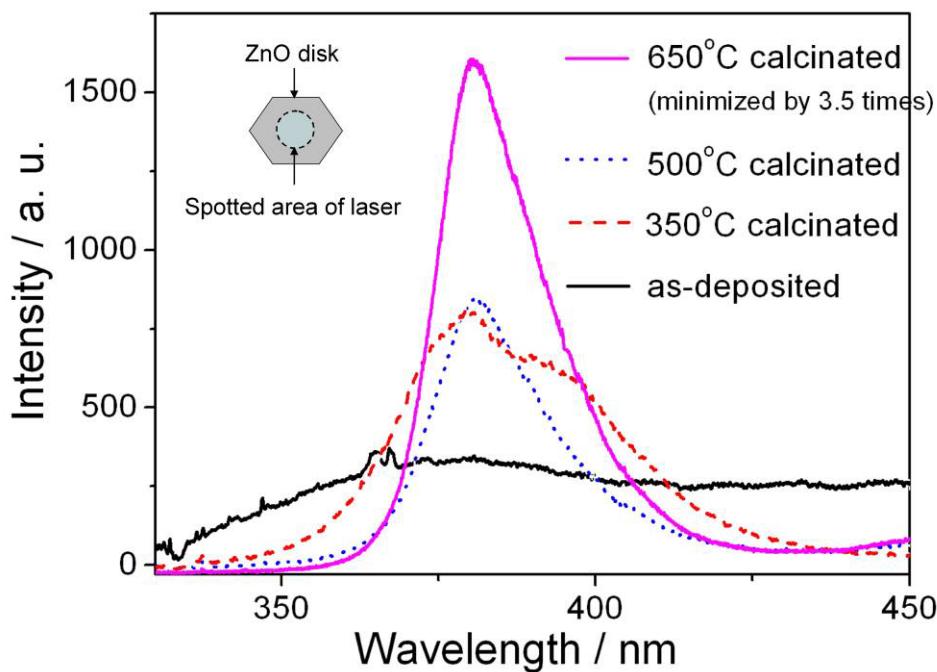
**Figure S2.** XPS spectrum of nanocrystalline ZnO hexagonal disks deposited on Si substrate calcinated at 500°C for 4 hours. The analyzing area: 6mm x 8mm. (The binding energy of F1s is 686 eV for Al Ka source, where no obvious peak was detected in the spectrum.)



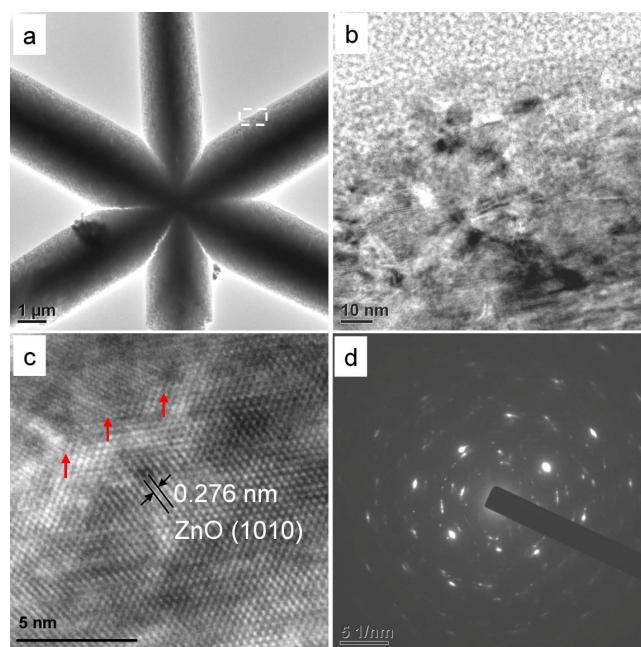
**Figure S3.** AES spectrum of a typical nanocrystalline ZnO hexagonal disks deposited on Si substrate calcinated at 500°C for 4 hours. The analyzing area is 2 um in diameter.



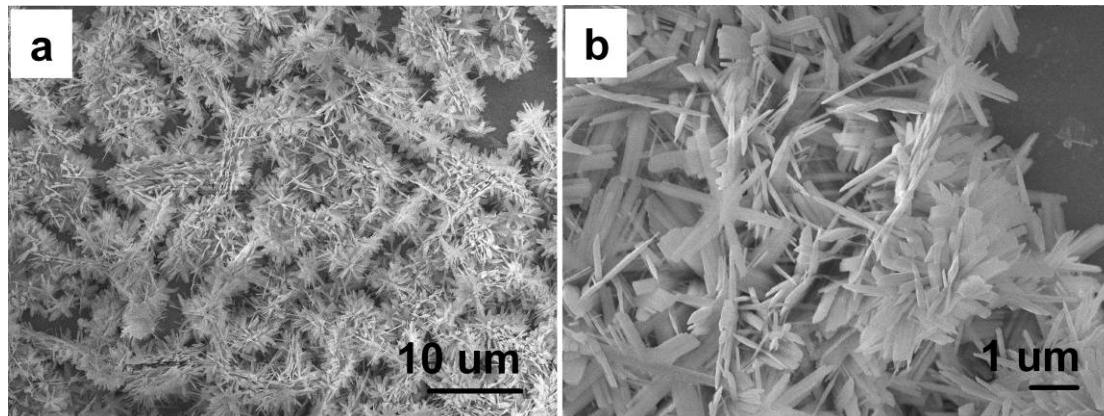
**Figure S4.** Photoluminescence spectra of nanocrystalline ZnO hexagonal disks deposited on Si substrate calcinated at different temperature (350-650°C) for 4 hours. The laser shot is ~ 2 um, with the wavelength of 325 nm from a He-Cd laser source.



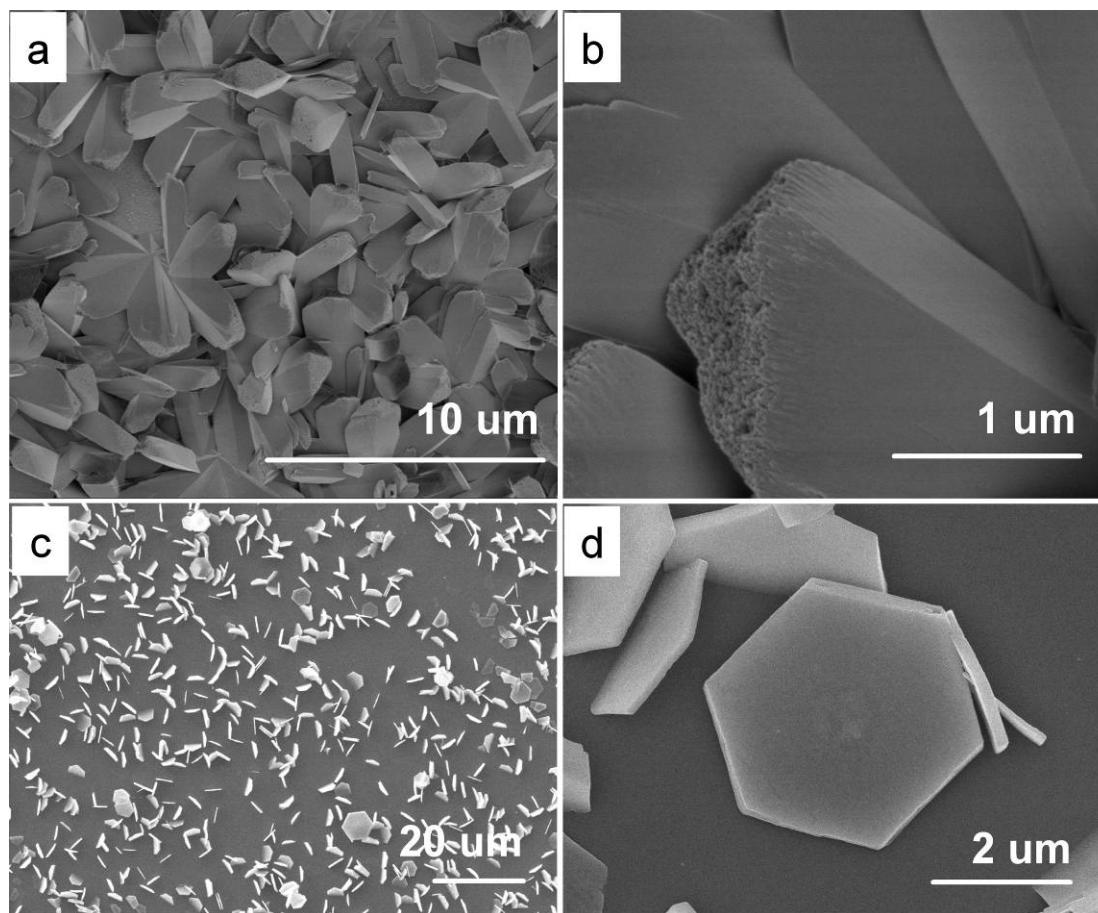
**Figure S5.** TEM images of nanocrystalline ZnO hexapods calcinated at 650°C for 4 hours. a) overview of the full particle; b) magnified view of the fringe of the arm, indicating the size of ZnO crystallites; c) high-resolution TEM image illustrating the lattice of ZnO crystallite and the grain boundary (indicated by the red arrows); d) SAED pattern, the diffraction spots indicate the ordered arrangement of ZnO nanocrystallites on the nanometer level.



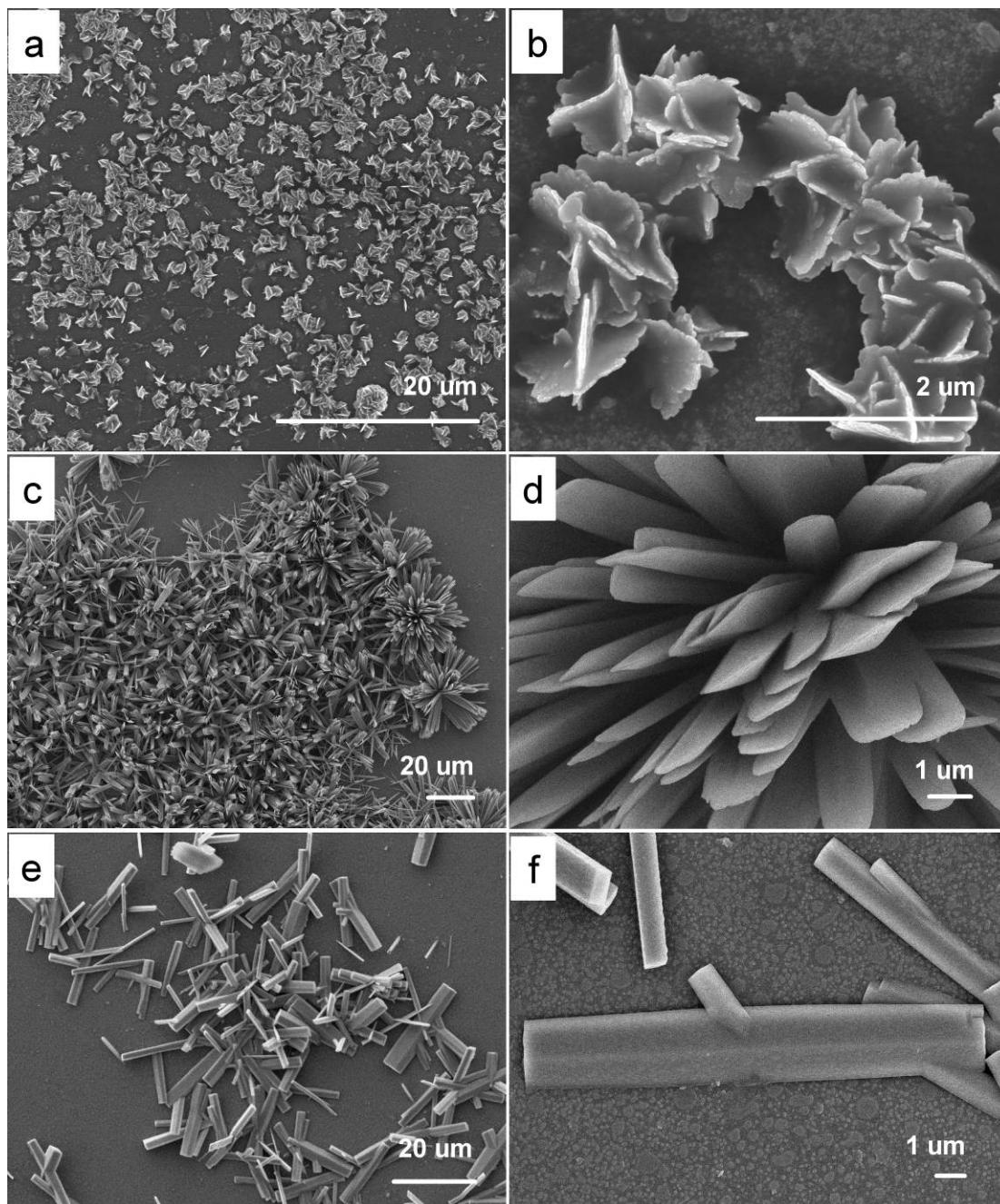
**Figure S6.** SEM images of eroded morphology of ZHC nanodisks deposited on Si substrate after immersing in NH<sub>4</sub>F solution at 70°C for 1 hour with H<sub>2</sub>O-ethonal component solvent (1:1 by volume). a) Low resolution image; b) Magnified view of Zn(OH)F nanobelts.



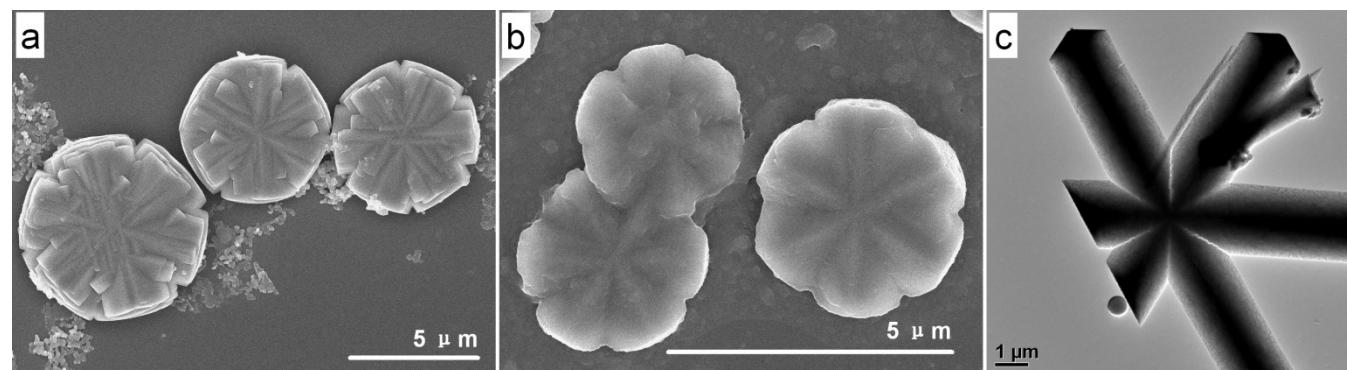
**Figure S7.** SEM images of Zn(OH)F (a and b) and ZHC (c and d) crystals deposited on glass substrates, with a) and c) for low resolution images and b) and d) for magnified view of each particle. For Zn(OH)F, no well-defined and well-distributed morphology were obtained. For ZHC, no assembly of nanodisks occurred.



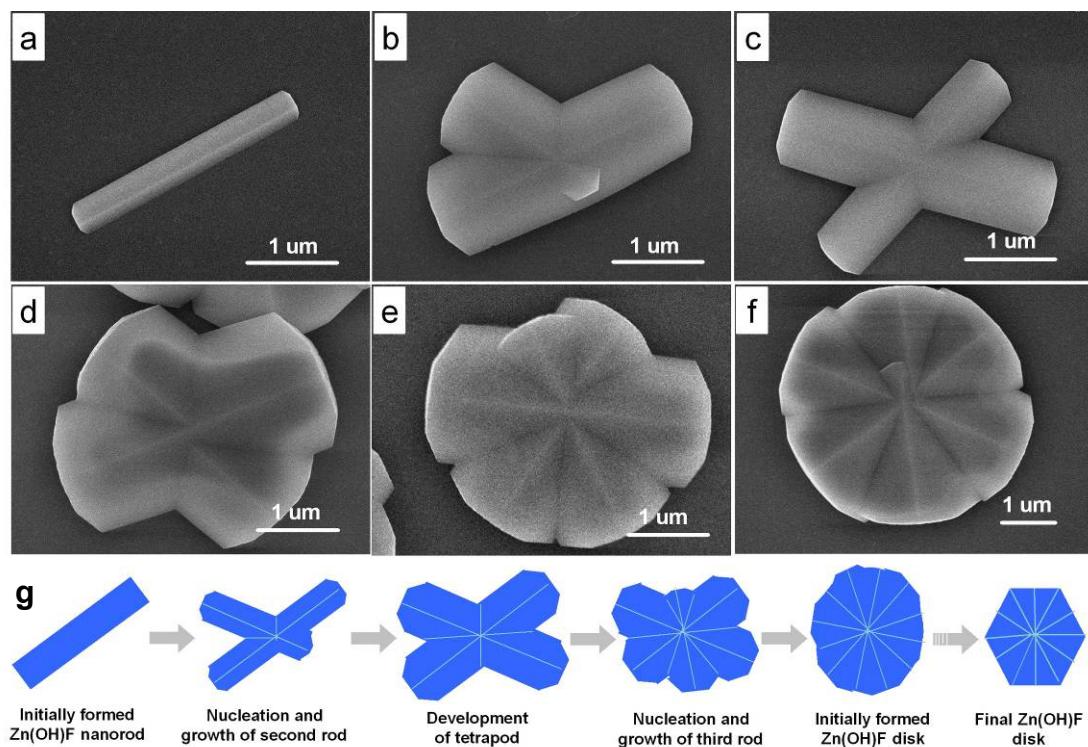
**Figure S8.** SEM images of Zn(OH)F nanostructures deposited on Si substrates. a-b) pure water solvent, at 70°C; c-d) pure water solvent, at 95°C; e-f) water-ethanol component solvent (9 : 1 by volume), at 70°C. a), c) and e) are low-resolution images, and b), d) and f) are high resolution ones.



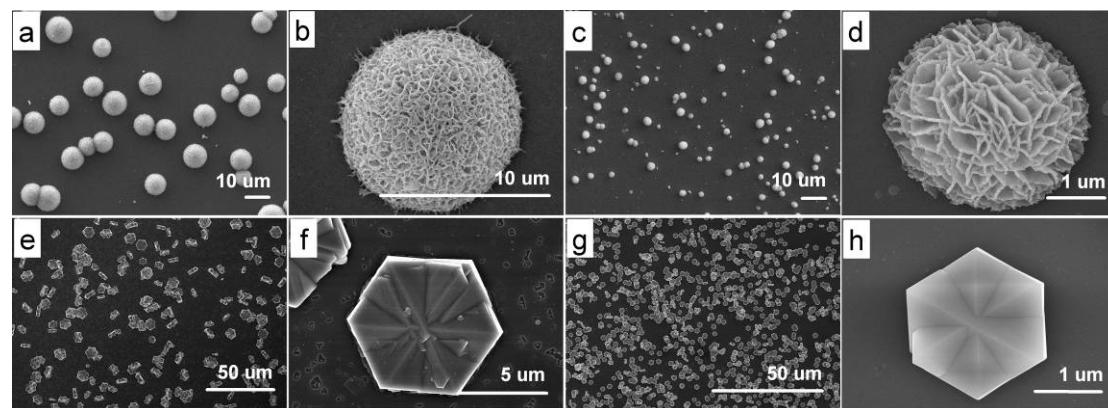
**Figure S9.** SEM images of Zn(OH)F crystals formed in the solution phase (a) and on the substrate (b) arrested at the initial stage of the reaction (5 minutes at 70°C). (c) TEM image of ZnO hexapods peeled from the substrate, indicating that the self-assembled process may occur in the solution phase as well.



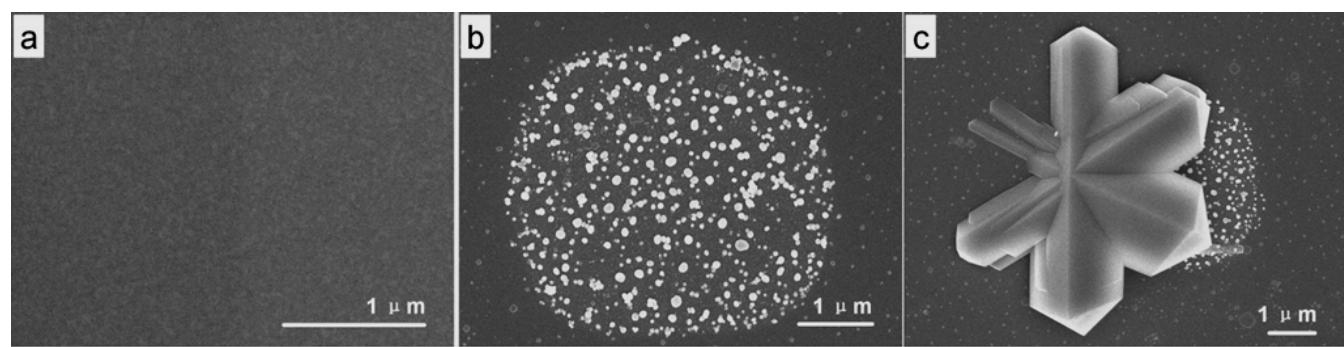
**Figure S10.** SEM images of Zn(OH)F hexagonal disk formed at the initial stage (10 minutes), illustrating the formation process of the hexagonal disk. a) single Zn(OH)F rod; b) tripods, showing the nucleation and growth of the second rod; c) initially formed tetrapods; d) fully-developed tetrapods; e) initially formed hexapods; f) fully-developed hexapods; g) the formation process of an individual Zn(OH)F hexagonal disk.



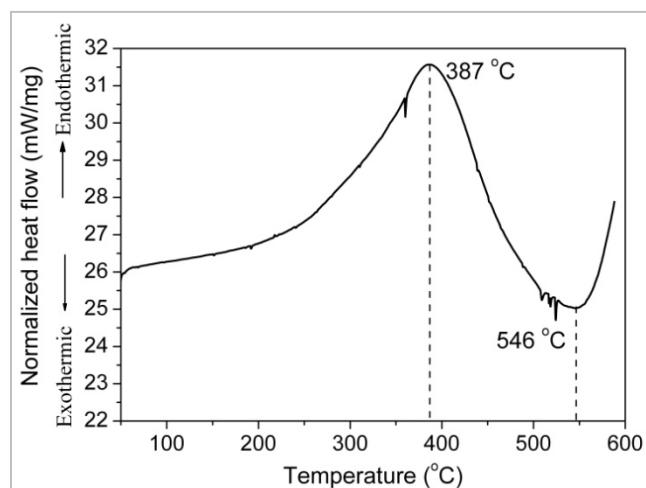
**Figure S11.** SEM images of Zn(OH)F sphere and hexagonal disk with different size, by varying the dosage of diluted hydrochloric acid added to the precursor. The concentration of HCl in precursor was 0.02 mol/l for large size and 0.014 mol/l for smaller size, respectively. a) and b) sphere with the diameter of 10  $\mu\text{m}$ ; c) and d) sphere with the diameter of 3.5  $\mu\text{m}$ ; e) and f) hexagonal disk with the size of 9  $\mu\text{m}$ ; g) and h) hexagonal disk with the size of 2.2  $\mu\text{m}$ .



**Figure S12.** SEM images of gold film before (a) and after (b) the thermal annealing at 600°C. (c) ZnO hexapods grown on the gold nanoparticles.



**Figure S13.** Differential scanning calorimetry (DSC) curve of Zn(OH)F powders accumulated in the solution phase with the typical mixture of Zn(OH)F disks ( $[ZnCl_2] = 0.03 \text{ mol/l}$ ,  $[F^-] = 5.26 \text{ mmol/l}$ ). The curve was obtained from Perkin Elmer Diamond DSC system, with the heating rate of  $20 \text{ }^\circ\text{C/min}$  and the temperature range of  $50\text{--}600 \text{ }^\circ\text{C}$ . The sample was  $0.8 \text{ mg}$  in weight.



**Figure S14.** SEM images of ZnO nanostructures with one pod grown firmly on the substrate, illustrating the good adhesion between ZnO nanostructures and Si substrate.

