Supporting Information

Morphology-tunable synthesis of ZnO nanoforest and its photoelectrochemical performance

Xing Sun,[a,#] Qiang Li,[a,b,#] Jiechao Jiang[c] and Yuanbing Mao[a,*]

[a]*Department of Chemistry, The University of Texas - Pan American, Edinburg, TX 78539 USA*
[b]*Department of Mechanical Engineering, The University of Texas - Pan American, Edinburg, TX 78539 USA*
[c]*Materials Science and Engineering Department, The University of Texas at Arlington, Arlington, TX, 76019 USA*
[#]*Both authors contributed equally to this work*
**To whom correspondence should be addressed: Phone: +1 956 665 2417; Fax: +1 956 665 5006; E-mail: maoy@utpa.edu*

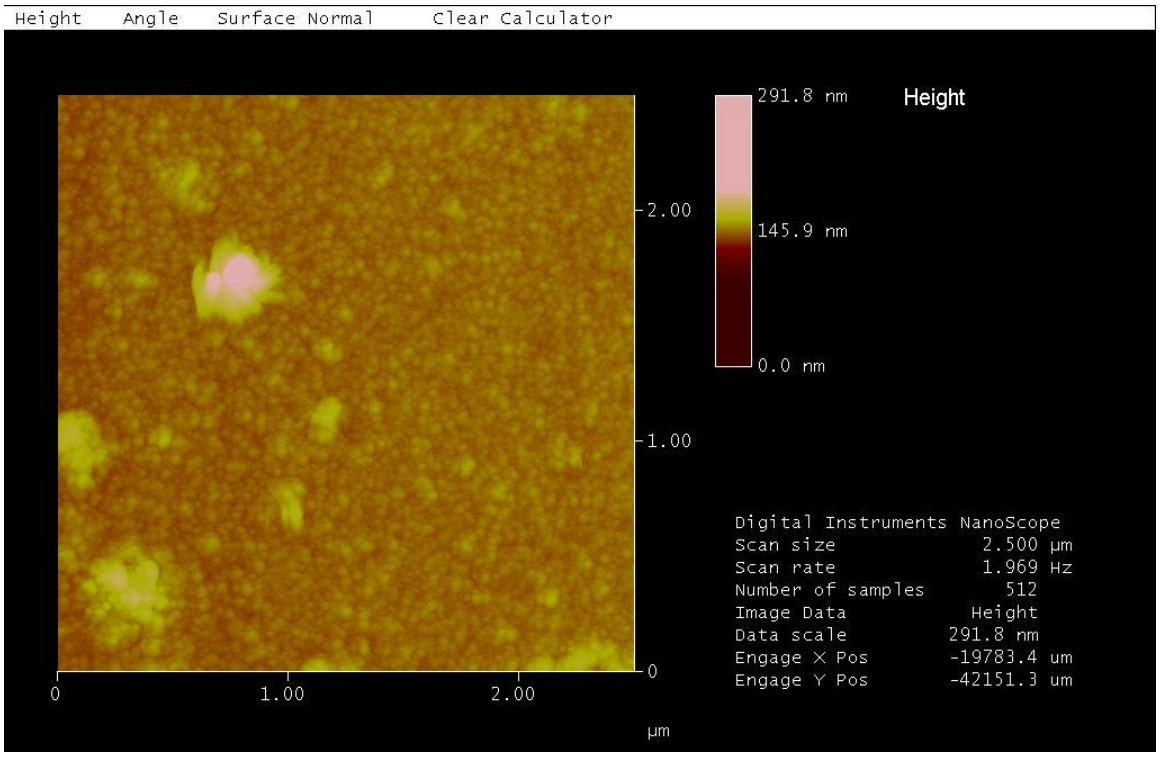

Fig. S1 AFM image of the surface of a glass substrate seeded by ZnO nanoparticles.

The atomic force microscopy (AFM) image of the surface of a glass substrate seeded by ZnO nanoparticle solution (shown in Fig. S1) displays the surface morphology of ZnO seed layer on the glass substrate after spin-coating. Those ZnO nanoparticles with a narrow size distribution (around 20-30 nm in diameter) were scattered over the surface.

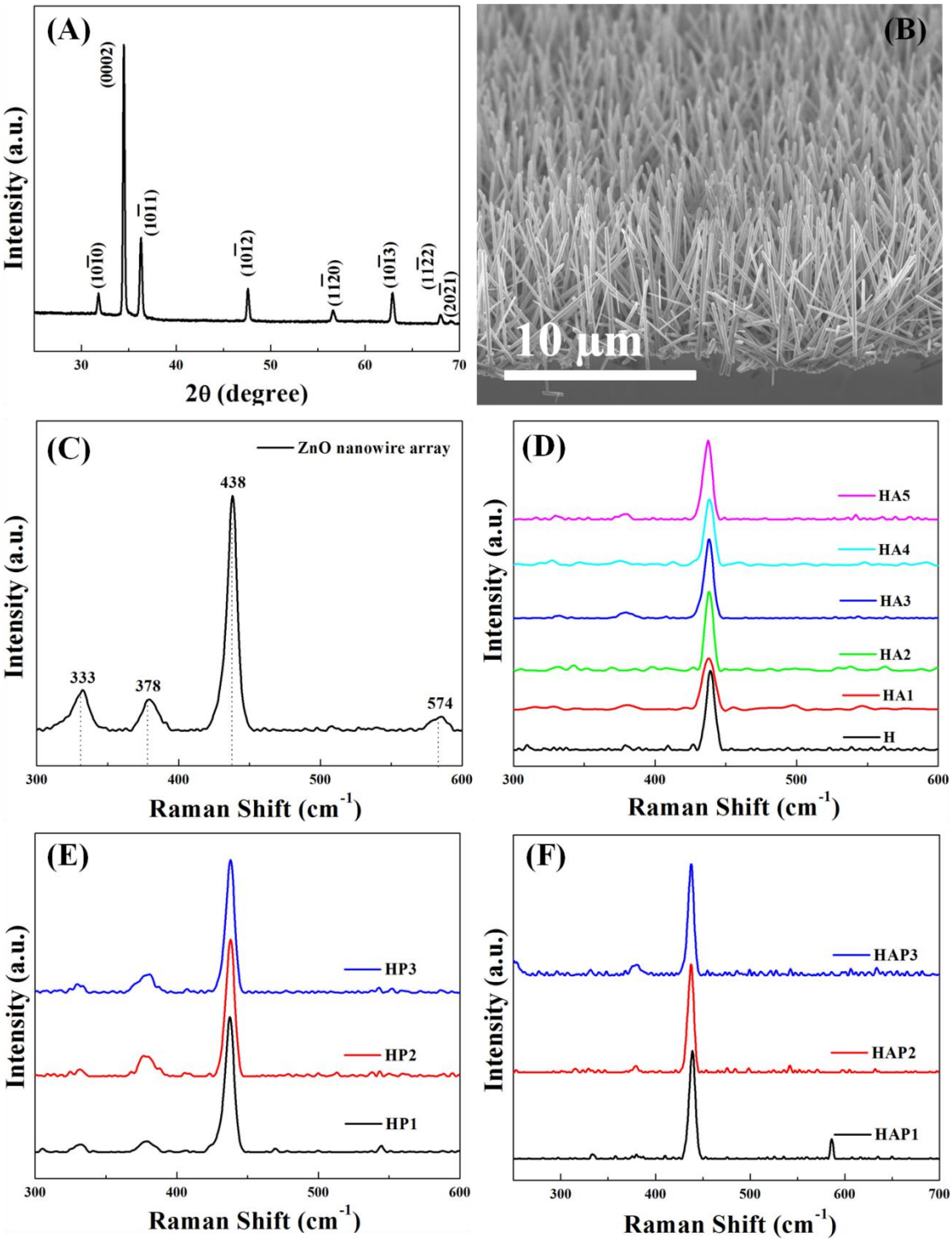

Fig. S2 (A) XRD pattern, (B) SEM image, and (C) Raman spectrum of the as-prepared ZnO nanowire arrays; (D-E) Raman spectra of ZnO nanoforests prepared under different concentrations of ammonia and/or PEI with the same labels as in the main text.

The phase purity, crystal structure, and vibrational mode of the as-prepared ZnO nanowire arrays were examined by XRD and Raman spectroscopy. In the XRD pattern of as-prepared ZnO nanowire arrays (Figure S2A), all the peaks are indexed to hexagonal wurtzite ZnO (JCPDS Card No. 36-1451) without other impurity peaks, indicating that the product is pure ZnO. Not only because <0002> is the dominant direction for crystal growth of ZnO nanowires, but they also grow vertically from the substrate in the direction of *c*-axis. In the XRD pattern, the highest peak is 0002 diffraction and the rest peaks recognized are $10\bar{1}0$, $10\bar{1}1$, $10\bar{1}2$, $11\bar{2}0$, $10\bar{1}3$, $11\bar{2}2$, and $20\bar{2}1$ diffraction. SEM images of as-prepared ZnO nanowire arrays in Fig. S2B, reveals that the nanowires vertically stand on the substrate, with ~150 nm diameter and ~7.5 μm length. The structure of ZnO nanowire arrays were characterized by Raman spectrum, shown in Fig. S2C. a strong Raman band at 438 cm^{-1} correspond to a non-polar E_2 vibration mode of wurtzite phase ZnO. Stronger E_2 than the 574 cm^{-1} band, suggests a good crystallinity of pristine ZnO nanowires, because the broad peak at 574 cm^{-1} is usually enhanced by disorder.[1,2] The XRD pattern, Raman spectrum and SEM image of ZnO nanowire arrays consistently demonstrate the preferential crystal growth direction and orientation of those nanostructures-along *c*-axis direction.[3-5]

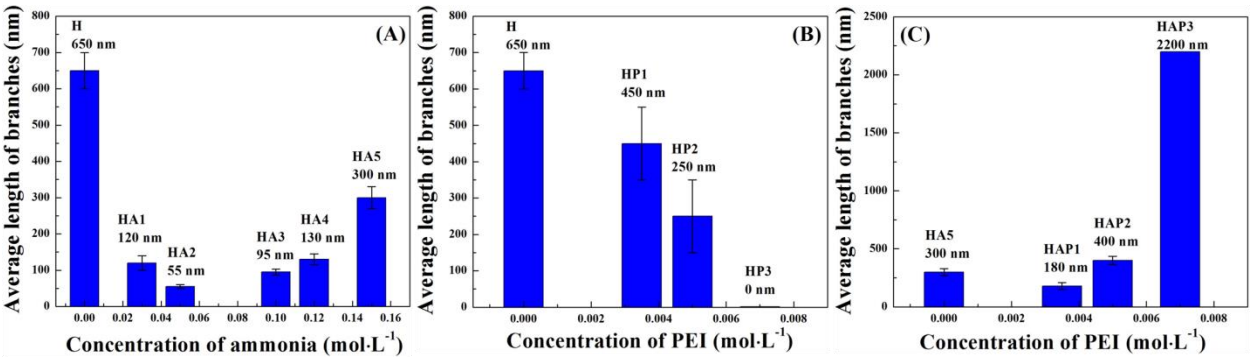

Fig. S3 Diagrams of branch length transitions with (A) increasing ammonia concentration, (B) increasing PEI concentration, (C) 0.15 M of ammonia and gradually increasing PEI concentration.

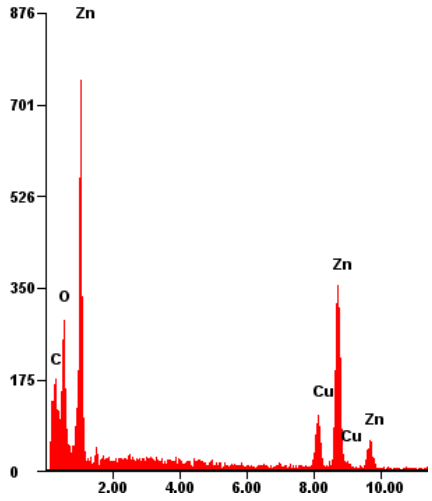

Fig. S4 EDS spectrum of as-prepared ZnO nanotrees.

The EDS spectrum in Fig. S4 demonstrated that the product is pure ZnO crystal without other impurities. The Cu peaks came from the copper grid.

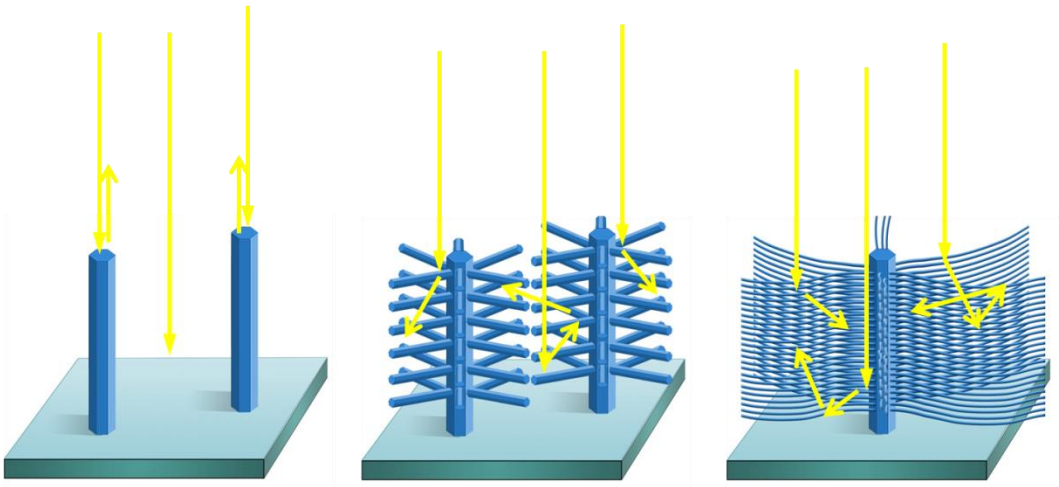

Fig. S5 Schematic of the light trapping on the surfaces of ZnO nanowires and nanoforests.

Reference

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[5] T. L. Sounart, J. Liu, J. A. Voigt, M. Huo, E. D. Spoerke, B. McKenzie, *J. Am. Chem. Soc.* **2007**, *129*, 15786.