†Supporting Information

Spontaneous hyper-branching in ZnO nanostructures: morphology dependent electron emission and light detection

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Characterization

Product morphology was investigated with a field emission scanning electron microscope (FESEM, HITACHI S-4800). Crystallinity and phase of the synthesized artifacts were characterized by X-ray diffraction (XRD, D8 Advanced Bruker) and high resolution transmission electron microscope (HRTEM, JEM 2100). Further phase purity and surface composition of the samples were inspected by X-ray photoelectron spectroscopy (XPS) using a SPECS HSA-3500 hemispherical analyzer with monochromatic Mg Kα x-ray source. Raman spectroscopic characterization was performed with WITec alpha 300RA Raman Confocal Microscope with 532 nm diode laser. The Brunauer–Emmett–Teller (BET) surface area of the heterostructures was measured with Quantachrome NovaWin2 Instrument.

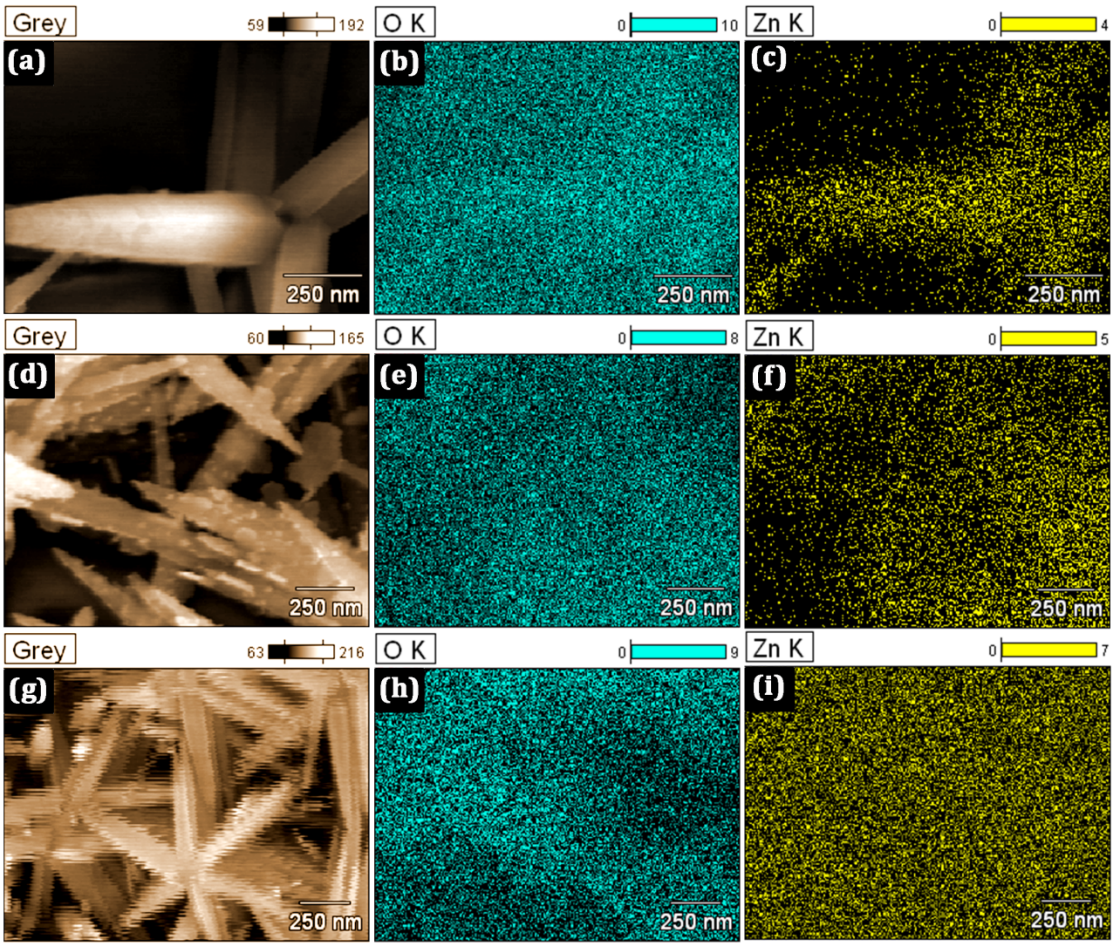

Fig S1: Elemental mapping of ZnO (a-c) nanospike, (d-f) nanocactus, and (g-i) nanotree.

Table S1† Comparison with the reported field emitters

Nanostructures	Turn-on field (V μm^{-1})	Threshold filed (V μm^{-1})	Field enhancement factor (β)	References
ZnO Nanowires	15.5 and 9.5 ($0.1\mu A/cm^2$)	—	1188 and 1334	1
ZnO Nanowires grown on C cloth	0.7 (1 mA/cm^2)	—	4.11×10^4	2
ZnO Nanowires	6.0 ($0.1\mu A/cm^2$)	—	847	3
ZnO radial nanowire array	1.3 ($0.1\ \mu A/cm^2$)	4.4 ($1mA/cm^2$)	3010	4
ZnO nanosheet on ITO	3.6 ($0.1\mu A/cm^2$)	—	4700	5
ZnO Nanotubes	7($0.1\mu A/cm^2$)	—	910	6
ZnO Nanoneedles	0.85 ($0.1\mu A/cm^2$)	—	8328	7
ZnO Nanorod	4.6	9.5	2923	8
Hierarchical nanosheet	3.5	7.3	4026	8
ZnO Nanobelts or nanoribbons	1.3	—	1.4×10^4	9
ZnO Nanoneedles	4.2	—	2350	10
ZnO Nanoneedles	2.5	—	—	11
ZnO Nanorods	4.1 ($0.1\mu A/cm^2$)	—	—	12
3D urchin-like ZnO nanostructure	3. 7	4. 8	1239	13
ZnO Nanowire	9.5	—	1334	14
ZnO Nanonails ZnO nanopencils	7.9 7.2	—	—	15
ZnO Nanoscrews	3.6	—	—	16
pin-cushion cactus like ZnO nano-pencil film	1.38 (0.1 $\mu A/cm^2$)	2.84 (49 $\mu A/cm^2$)	—	17
ZnO NWs/graphene	2.4	—	5661	18
ZnO nanospike	3.01	—	4473	
ZnO Nanocactus	1.44	4.10	14619	This work
ZnO Nanotree	2.03	5.09	8771	

We define the turn-on and threshold field at a field producing emission current density of 10 μA/cm^2 and 1mA/cm^2 respectively. If other values are used, this is mentioned separately.

Table S2† Comparison with the reported UV detectors

Nanostructures	Dark current (I_d) (A)	Photocurrent (I_{ph}) (A)	Gain	Reference
ZnO hollow sphere Nanofilm	50×10^{-9}	2.6×10^{-6}	53	19
ZnO NR	—	2.4×10^{-6}	10^3	20
ZnO nanowire by chemical route	$\sim15\times10^{-12}$	0.28×10^{-9}	19.66	21
ZnO nanowires	5.98×10^{-10}	4.67×10^{-6}	7.8×10^3	22
Sputtered ZnO film	1.01×10^{-10}	1.11×10^{-4}	1.1×10^6	
ST ZnO NW	0.04×10^{-9}	60×10^{-9}	1500	23
ZnO NW array	70×10^{-6}	100×10^{-6}	—	24
ZnS /ZnO nanobelt	3.03×10^{-6}	17.76×10^{-6}	6.86	25
Hierarchical nanosheet	5.12×10^{-11}	1×10^{-5}	1.95×10^5	8
Cu- ZnO NW	10×10^{-12}	100×10^{-9}	7000	26
ZnO nanowires, ZnO-PVA nano-composite	5.2×10^{-10} 1.35×10^{-9}	9.7×10^{-6} 6.52×10^{-5}	1.8×10^4 4.8×10^4	27
ZnO NW	20×10^{-9}	140×10^{-9}	—	28
ZnO nanowire by Vapor phase	8.2×10^{-8}	2.8×10^{-6}	35.146	29
ZnO thin film by sol–gel	8.29×10^{-9}	5.01×10^{-6}	606	30
ZnO Nanowire coated with ZnS	6.0×10^{-8}	2.02×10^{-4}	3367	31
ZnO Nanowire	1.29×10^{-8}	1.42×10^{-5}	1.1×10^3	32
ZnO Nanorod	5.34×10^{-10}	9.56×10^{-8}	1.8×10^2	
ZnO nanospike	9.91×10^{-9}	3.26×10^{-7}	3.38×10^1	
ZnO Nanocactus	4.57×10^{-9}	1.12×10^{-6}	2.46×10^2	This work
ZnO Nanotree	1.63×10^{-10}	3.61×10^{-6}	2.21×10^4	

REFERENCES

1) B. Q. Cao, X. Teng, S. H. Heo, Y. Li, S. O. Cho, G. Li and W. Cai, *J. Phys. Chem. C,* 2007, **111**, 2470.
2) D. Banerjee, S. H. Jo and Z. F. Ren, *Adv. Mater.,* 2004, **16**, 2028.

3) C. J. Lee, T. J. Lee, S. C. Lyu, Y. Zhang, H. Ruh and H. J. Lee, *Appl. Phys. Lett.,* 2002, **81**, 3648.

4) F. Xu, K. Yu, G. Li, Q. Li and Z. Zhu, *Nanotechnology,* 2006, **17**, 2855.

5) D. Pradhan, M. Kumar, Y. Ando and K. T. Leung, *Nanotechnology,* 2008, **19**, 035603:1.

6) A. Wei, X. W. Sun, C. X. Xu, Z. L. Dong, M. B. Yu and W. Huang, *Appl. Phys. Lett.,* 2006, **88**, 213102:1.

7) C. J. Park, D. K. Choi, J. Y. Yoo, G. C. Yi and C. J. Lee, *Appl. Phys. Lett.,* 2007, **90**, 083107:1.

8) S. Maiti, U. N. Maiti and K. K. Chattopadhyay, *CrystEngComm,* 2012, **14**, 8244.

9) W. Z. Wang, B. Q. Zeng, J. Yang, B. Poudel, J. Y. Huang, M. J. Naughton and Z. F. Ren, *Adv. Mater.,* 2006, **18**, 3275.

10) J. P. Liu, X. T. Huang, Y. Y. Li, X. X. Ji, Z. K. Li, X. He and F. L. Sun, *J. Phys. Chem. C* 2007, **111**, 4990.

11) Y. B. Li, Y. Bando and D. Golberg, *Appl. Phys. Lett.,* 2004, **84**, 3603.

12) Q. Zhao, X. Y. Xu, X. F. Song, X. Z. Zhang, D. P. Yu, C. P. Li and L. Guo, *Appl. Phys. Lett.,* 2006, **88**, 033102:1.

13) H. Jiang, J. Hu, F. Gu and C. Li, *Nanotechnology,* 2009, **20**, 055706:1.

14) X. Fang, Y. Bando, U. K. Gautam, C. Ye and D. Golberg, *J. Mater. Chem*., 2008, **18**, 509.

15) S. J. Chen, Y. C. Liu, C. L. Shao, R. Mu, Y. M. Lu, J. Y. Zhang, D. Z. Shen and X. W. Fan, *Adv. Mater.,* 2005, **17**, 586.

16) L. Liao, J. C. Li, D. H. Liu, C. Liu, D. F. Wang, W. Z. Song and Q. Fu, *Appl. Phys. Lett.,* 2005, **86**, 083106:1.

17) S. S. Warule, N. S. Chaudhari, J. D. Ambekar, B. B. Kale and M. A. More, *ACS Appl. Mater. Interfaces,* 2011, **3**, 3454..

18) J. O. Hwang, D. H. Lee, J. Y. Kim, T. H. Han, B. H. Kim, M. Park, K. No and S. O. Kim, *J. Mater. Chem.,* 2011, **21**, 3432.

19) M. Chen, L. Hu, J. Xu, M. Liao, L. Wu and X. Fang, *Small*, 2011, **7**, 2449.

20) J. Y. Park, Y.S. Young, Y.S. Hong, H. Oh, J. J. Kim and S. S. Kim, *Appl. Phys. Lett.,* 2005, **87**, 123108:1.

21) S-E. Ahn, H. J. Ji, K. Kim, G. T. Kim, C. H. Bae, S. M. Park, Y-K. Kim and J. S. Ha, *Appl. Phys. Lett.,* 2007, **90**, 153106.

22) T. Ghosh and D. Basak, *Nanotechnology,* 2010, **21**, 375202.

23) J. Zhou, Y. D. Gu, Y.F. Hu, W. J. Mai, P. H. Yeh, G. Bao, A. K. Sood, D. L. Polla and Z. L. Wang, *Appl. Phys. Lett.,* 2009, **94**, 191103:1.

24) J. B. K. Law and J. T. L. Thong, *Appl. Phys. Lett.,* 2006, **88**, 133114:1.

25) L. Hu, J. Yan, M. Liao, H. Xiang, X. Gong, L. Zhang and X. Fang, *Adv. Mater*., 2012, **24**, 2305.

26) N. Kouklin, *Adv. Mater.,* 2008, **20**, 2190.

27) A. Bera and D. Basak, *ACS Appl. Mater. Interfaces,* 2009, **1**, 2066.

28) Z. Y. Fan, D. Dutta, C. J. Chien, H. Y. Chen, E. C. Brown, P. C. Chang and J. G. Lu, *Appl. Phys. Lett.,* 2006, **89**, 213110:1.

29) S. Hullavarad, N. Hullavarad, D. Look and B. Claflin, *Nanoscale Res Lett*., 2009, **4**, 1421.

30) M. Dutta, S. Mridha and D. Basak, *Appl. Surf. Sci.,* 2008, **254**, 2743.

31) A. Bera and D. Basak, *ACS Appl. Mater. Interfaces,* 2010, **2**, 408.

32) S. Maiti, U. N. Maiti, A. Chowdhury and K. K. Chattopadhyay, *CrystEngComm,* 2014, **16**, 1659.