

Supplementary materials for “Rational Synthesis of P-type Zinc Oxide Nanowire

Arrays Using Simple Chemical Vapor Deposition”

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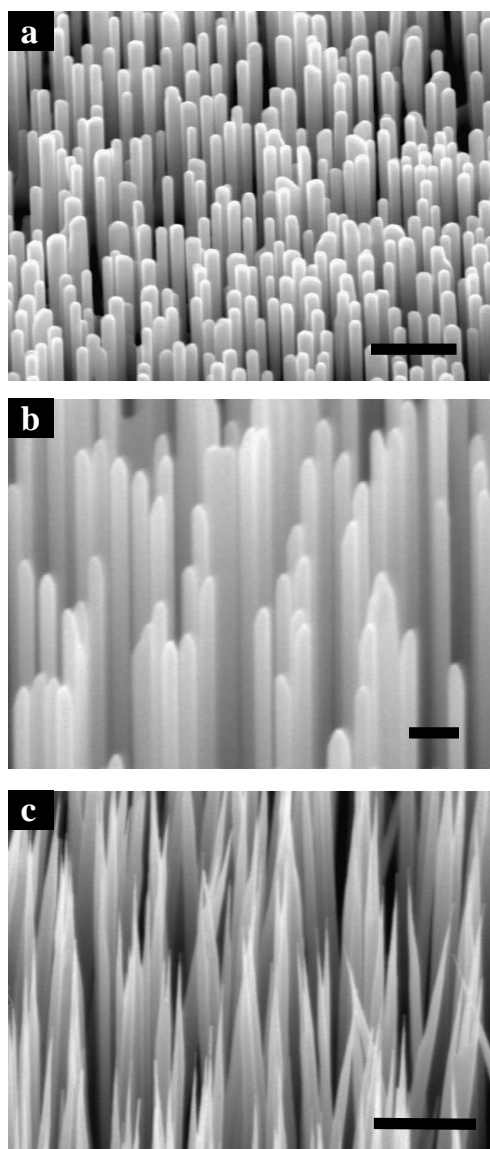


Figure S1. SEM images of the ZnO NWs synthesized with a different percentage of the P_2O_5 powder weight 0, 15%, and 30%, respectively. (a) SEM image of the ZnO NWs grown without P_2O_5 powder in the source ($ZnO + C$, 1:1 molar ratio). The image shows the flat top morphology of the as-grown ZnO NWs with diameter and length around 125 nm and 1.2 μm , respectively. Scale bar is 1 μm . (b) SEM image of the ZnO NWs prepared with 15% weight of P_2O_5 powder in the source mixture. NWs are much thinner but longer with diameter and length ~ 55 nm and 2 μm ,

respectively. NWs are slightly tapered at the end for about 30 – 40 nm. Scale bar is 200 nm. (c)

SEM image of the ZnO NWs grown with 30% weight of P_2O_5 powder in source. NWs are much more tapered and for the entire NW length, with diameter of around 180nm at root and 20 nm at tip. Scale bar is 1 μm .

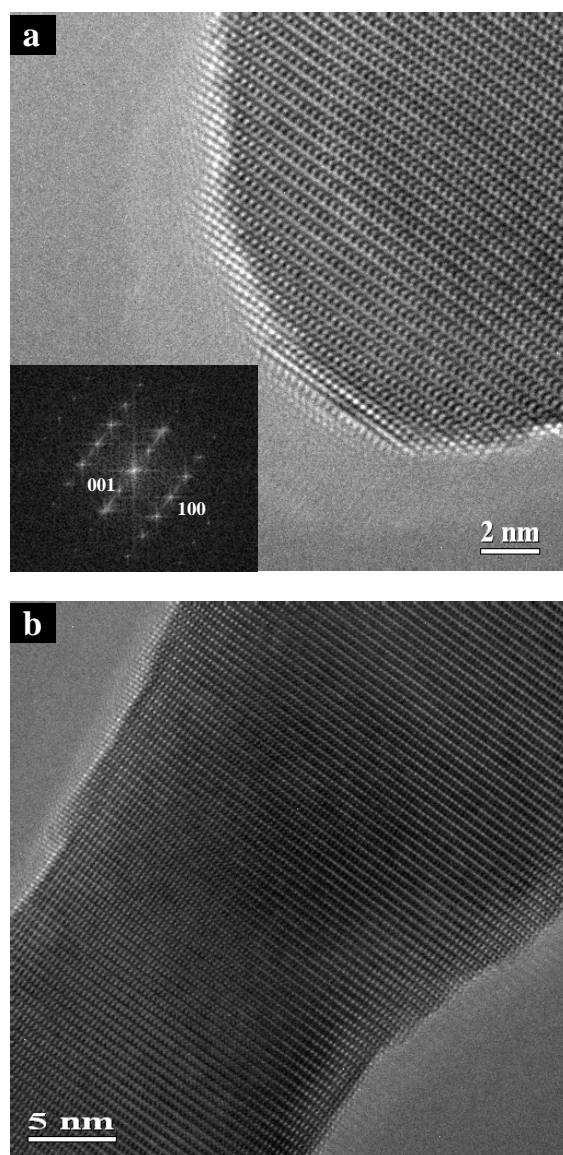


Figure S2. HRTEM images of top of ZnO:P NWs. (a) HRTEM image of the tip of ZnO:P NW.

Inset: The corresponding FFT. (b) HRTEM image of the neck of ZnO:P NW. The images show that the ZnO:P NWs are high-quality single crystal with growth axis along the $\langle 001 \rangle$ direction all

the way from body to the tip. And there is no phase charge, dislocation defects, or clusters in these ZnO:P NWs.

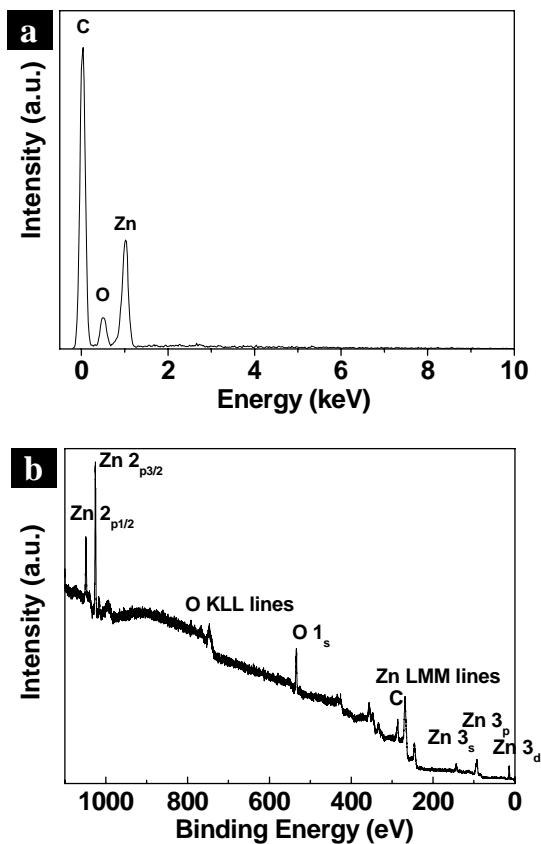


Figure S3. EDX and XPS analysis of the as-grown ZnO:P NWs (after annealing). (a) The EDX spectrum shows the chemical compositions of the ZnO NWs; there is no P element detected within the detection resolution. (b) XPS spectrum of the ZnO:P NWs. Only ZnO phase is obtained and there is no second phase peak or clusters observed.

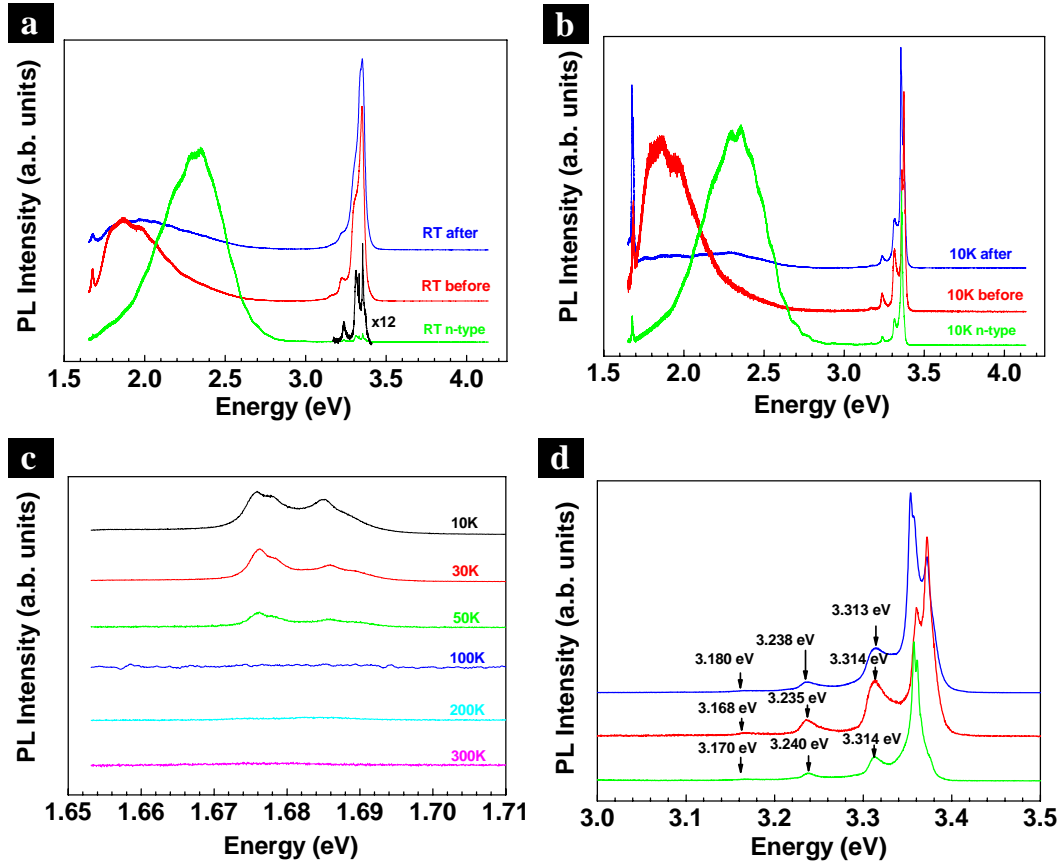


Figure S4. Photoluminescence studies of ZnO NWs. (a) Room temperature PL spectra. Green line shows strong green emission (oxygen vacancies)¹ and weak UV (band edge emission), black line is enlarged for 12 times; the as-grown ZnO:P NWs shows strong band edge emission in UV and broad red emission at 1.8eV, which has not been reported from P-doped ZnO in the literature, it most probably is due to the radioactive recombination of electrons in $[P_{Zn}-2V_{Zn}]$ complex formed from one P anti-site (P_{Zn}) and two Zn vacancies (V_{Zn}), whose $(2-/1-)$ transition are deep donors and have energy level of 2.79eV above valance band edge and predicted to be most stable and favorable acceptors for Zn_3P_2 dopant source,²⁰ and negatively charged substitutional P in O site (P_O^-) that is 0.93eV from the valance band maximum,^{1,15} after annealing at 850°C in nitrogen for 1 minute, the band edge emission is enhanced but the red emission is significantly quenched,

which is probably due to the decrease of defects during the annealing process (blue line). (b) Low temperature PL spectra at 10K of the n-type (green line), as grown ZnO:P (red line), and annealed (blue line) ZnO:P NWs. The band-edge emissions are enhanced at low temperature for all the three type of NWs. For annealed ZnO:P NWs, the red emission is further quenched at low temperature indicating the possible nonionization of charged dopant impurities. (c) The temperature-dependence PL spectra of the ZnO:P NWs after annealing for the peaks between 1.67eV and 1.69eV, which, also seen in Figs. S4a and S4b, are believed to be the second order peak of the excitonic emission and has similar features.^{S1} (d) The longitudinal optical (LO)-phonon replicas of excitons. For the ZnO:P NWs, the 3.31eV, 3.24eV 3.18eV peaks can be assigned as the 1st, 2nd and 3rd LO-phonon replicas of free exciton, 1LO(FX_A), 2LO(FX_A), and 3LO(FX_A), respectively.²⁶ The relative intensity of photon replicas agree with the exciton peak intensities for the as-grown and annealed ZnO:P NWs. The PL from the unintentionally doped ZnO NWs shows similar features but originated from different natures. The broad peaks at 3.31eV, 3.24eV, and 3.16eV can be assigned as the characteristic two-electron satellite (TES) level, which is intrinsically the excited state of the donor-bound-exciton, and the 1st and 2nd LO phonon replicas, respectively. Note the TES maybe overlapped with 1st LO phonon replicas of donor-bound-exciton, 1LO(D⁰₁X).

Reference

S1. Tseng, Y. K.; Hsu, H.C.; Hsieh, W.F.; Liu, K. S.; Chen, I. C. *J. Mater. Res.* **2003**, *18*, 2837.