

SUPPLEMENTARY INFORMATION

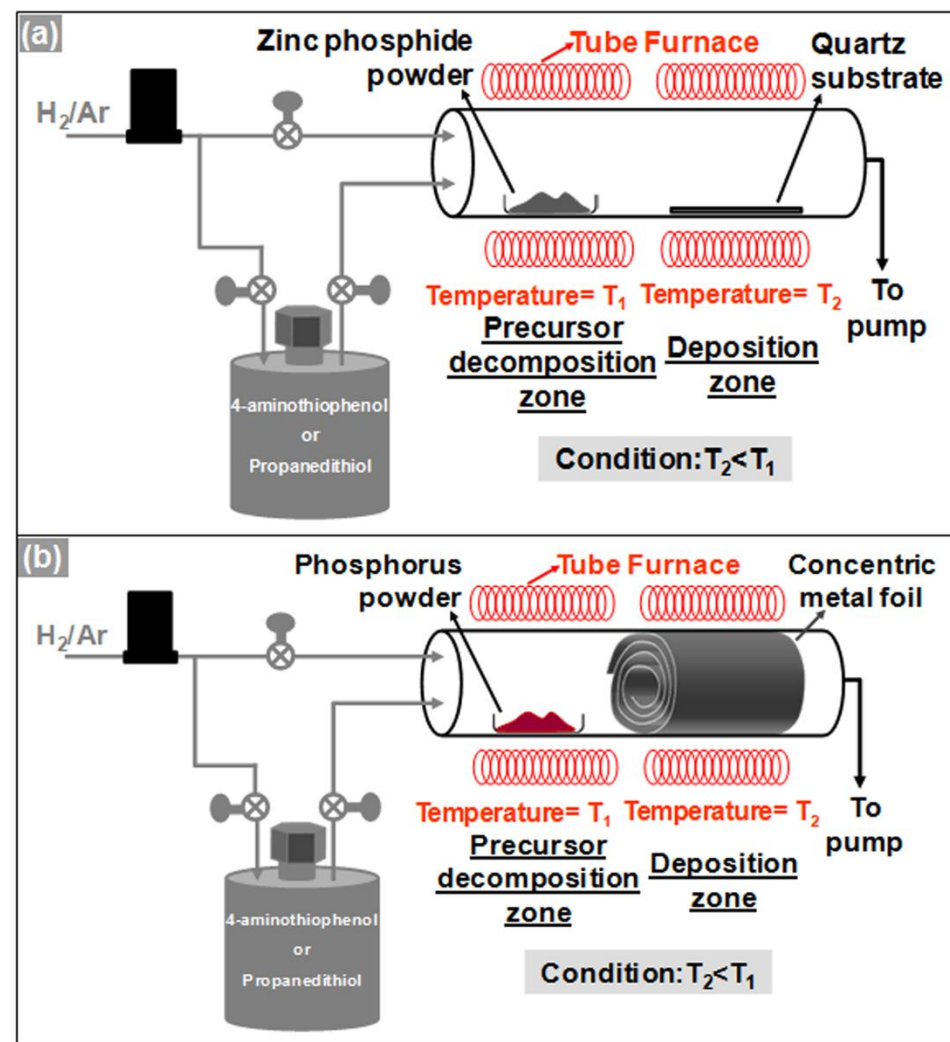


Figure S1. Schematic of the three-zone tube furnace employed for the synthesis and *in-situ* functionalization of Zn_3P_2 nanowires, indicating (a) the placement of the quartz substrate for the reactive vapor transport of zinc and phosphorus using Zn_3P_2 powder as the source for obtaining Zn_3P_2 nanowires on a small-scale (first experimental route), and (b) the placement of the coiled zinc foil employed for the large-scale synthesis of Zn_3P_2 nanowires using phosphorus vapor transport onto zinc foils (second experimental route).

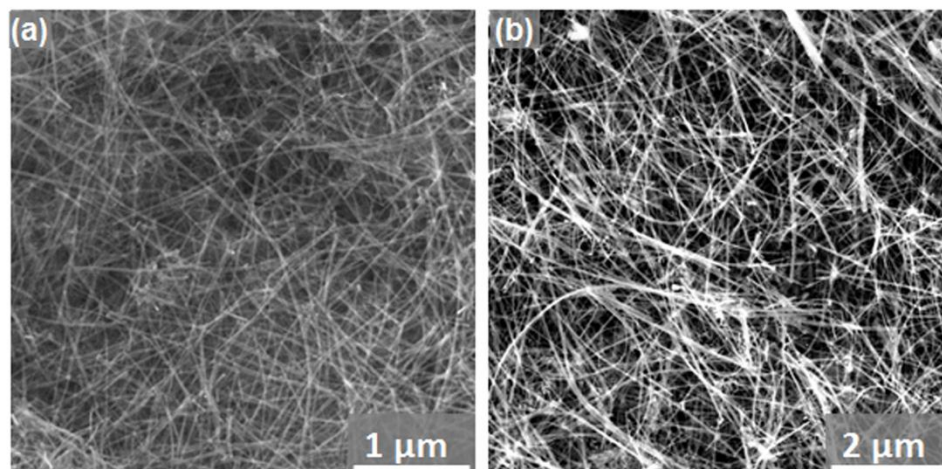


Figure S2. Morphologies of (a) Zn_3P_2 nanowires *in-situ* functionalized with 4-aminothiophenol synthesized using Zn_3P_2 powder as source on quartz substrate (first experimental route), and (b) Zn_3P_2 nanowires *in-situ* functionalized with 4-aminothiophenol synthesized using vapor transport of phosphorus onto zinc foils (second experimental route). In both the cases, *in-situ* functionalization did not impact the morphologies of the obtained nanowires.

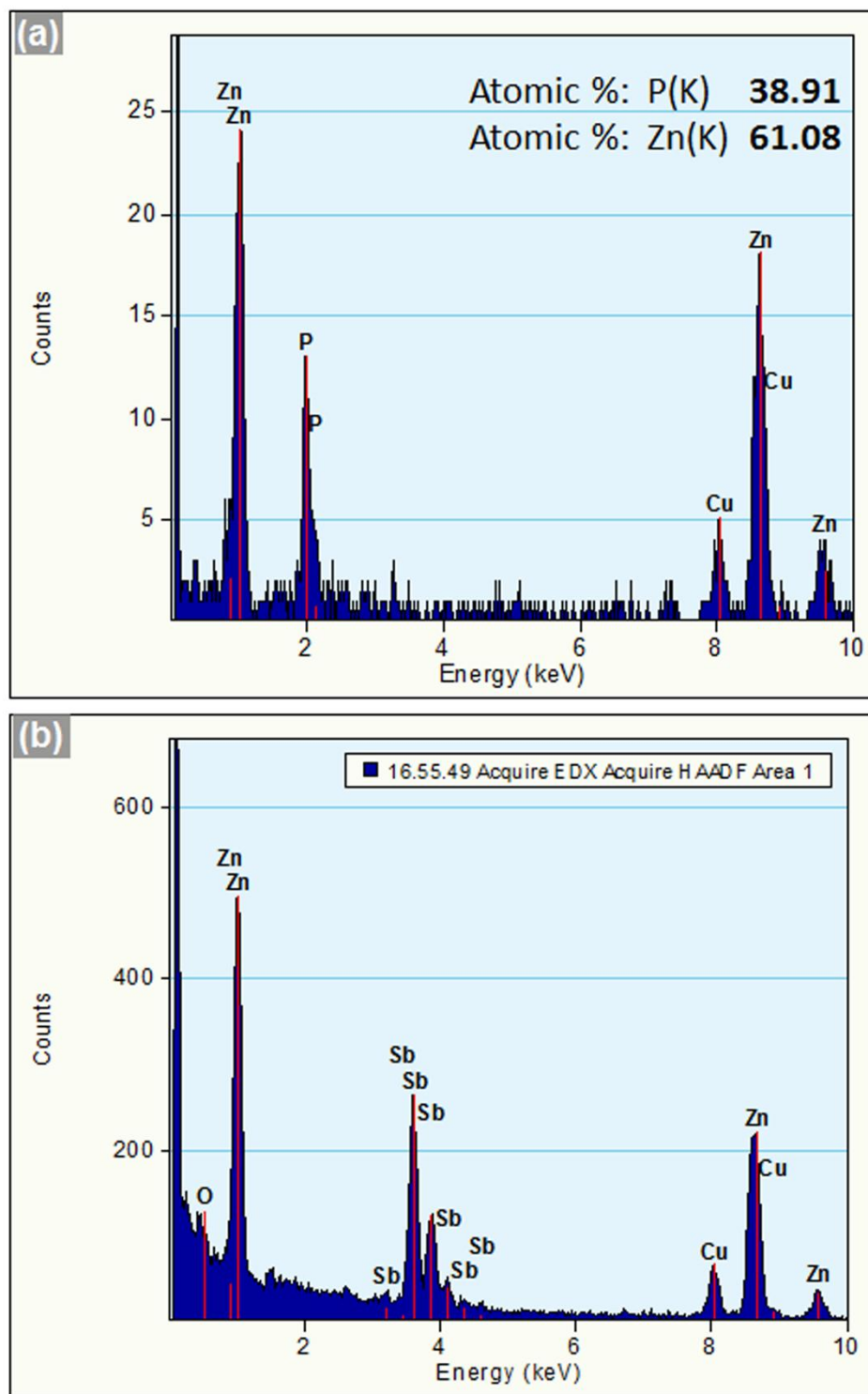


Figure S3. TEM-EDS analysis of (a) Zn₃P₂ nanowires and (b) Zn₄Sb₃ nanowires. The analysis indicated that in both the cases the nanowires are pure and devoid of any contaminants, such as chlorine.

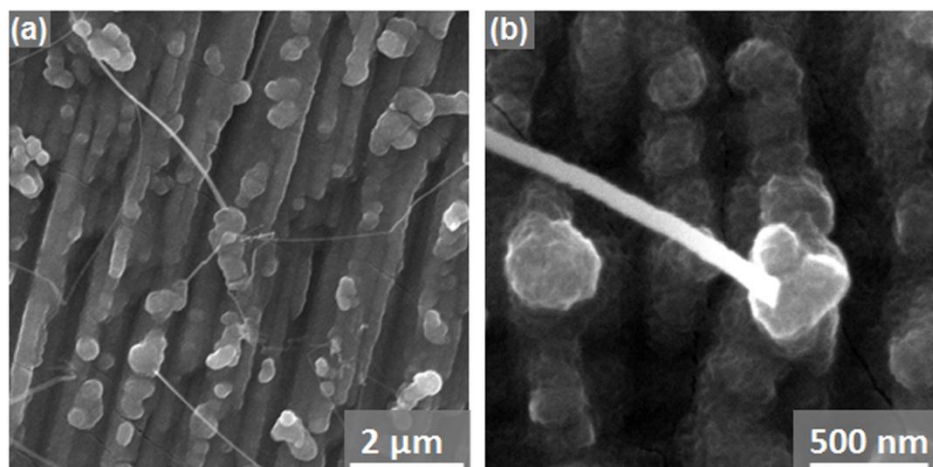


Figure S4. Scanning electron micrographs of a zinc foil after the vapor transport of phosphorus onto its surface for a short duration of 5 minutes. The formation of small Zn_3P_2 crystal nuclei preceded the formation of nanowires. This is indicative of the fact that self-catalysis via zinc droplets is responsible for the formation of nanowires.

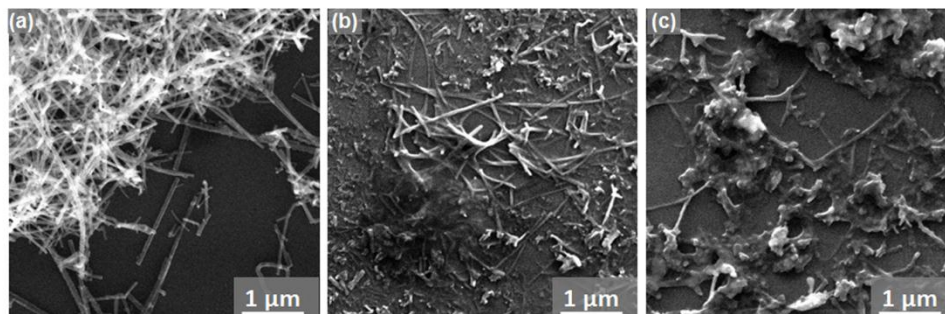


Figure S5. Scanning electron micrographs of Zn_3P_2 nanowires (a) *in-situ* functionalized with 3-propanedithiol, (b) *ex-situ* functionalized with 3-propanedithiol, and (c) unfunctionalized. These images were obtained after suspending the nanowires in THF for a period of 60 days. *In-situ* functionalized Zn_3P_2 nanowires did not exhibit signs of agglomeration and degradation, unlike *ex-situ* and unfunctionalized nanowires.