Electronic Supplementary Material (ESI) for Nanoscale.

Supplementary Material

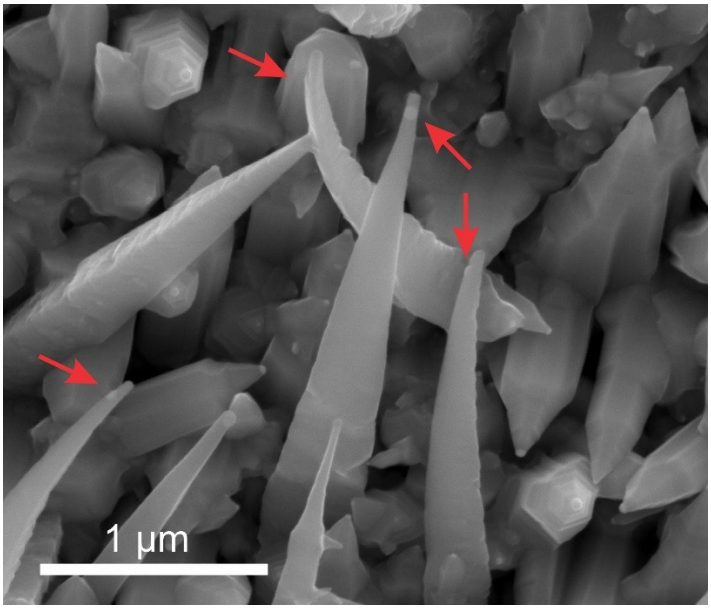

Figure S1. SEM image of the sample. The arrows point to the catalyst at the sidewall of the <211>-oriented nanowires, meanwhile the hexagonal nanowires can be identified by having their catalyst at nanowire tip.

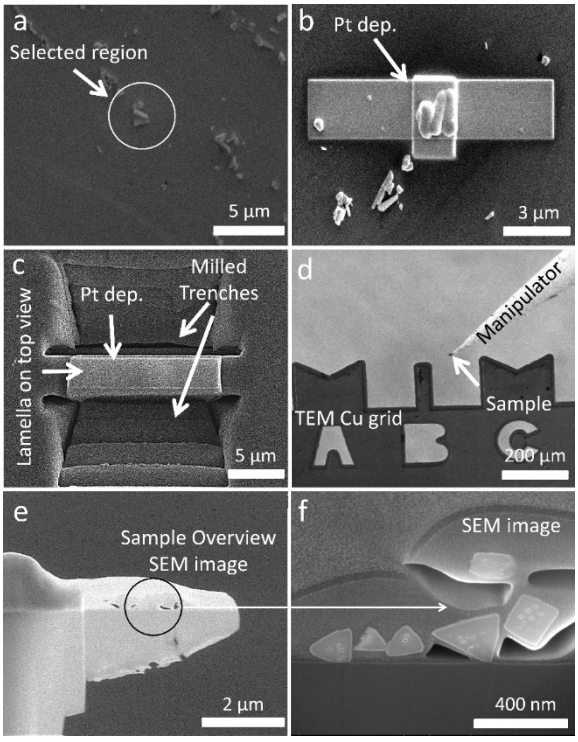

Figure S2: Images showing the details of the cross-section TEM sample preparation of the nanowires using a Dual Beam microscope. (a) Nanowires deposited on top of a silicon substrate. (b) In situ Pt deposition to

protect nanowires from ion beam damage in next steps. (c) Top view of the lamella after focused ion beam milling. (d) Transferring the lamella to the TEM grid using the Ominiprobe manipulator. (e) and (f) Cross-section SEM images of the nanowires ready to be analyzed in the TEM.

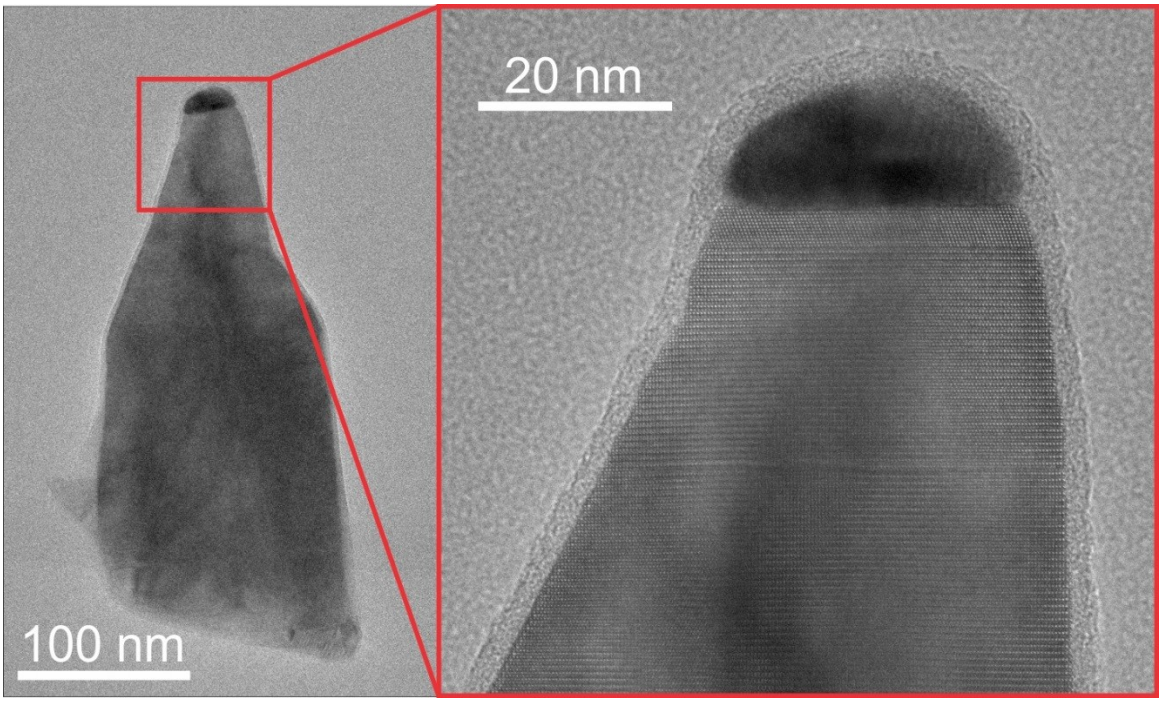

Figure S3. TEM image of a hexagonal nanowire. They are <111>-oriented, with wurtzite crystal structure and a zinc blende neck, characteristic from growth during temperature cool down.

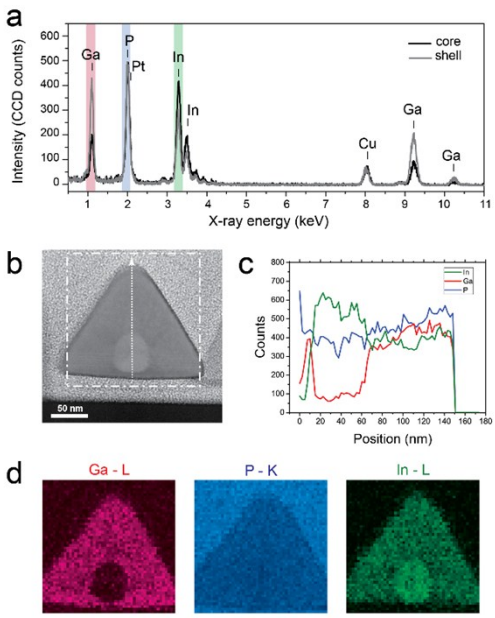

Figure S4: EDS analyzes on STEM mode of a FIB cross-section nanowire prepared with a DualBeam microscope. (a) EDS spectra acquired on the nanowire core (black) and shell (grey). (b) STEM HAADF image, where the dashed white arrow indicates the EDS line scan position, shown on (c), and the dashed white square indicates the EDS image area, showed on (d). The red, blue and green strips on (a) indicate the energy band used to analyze the Ga, P and In content, respectively. It is important to mention that the P map also shows Pt content out of the wire due to the EDS peak overlap.

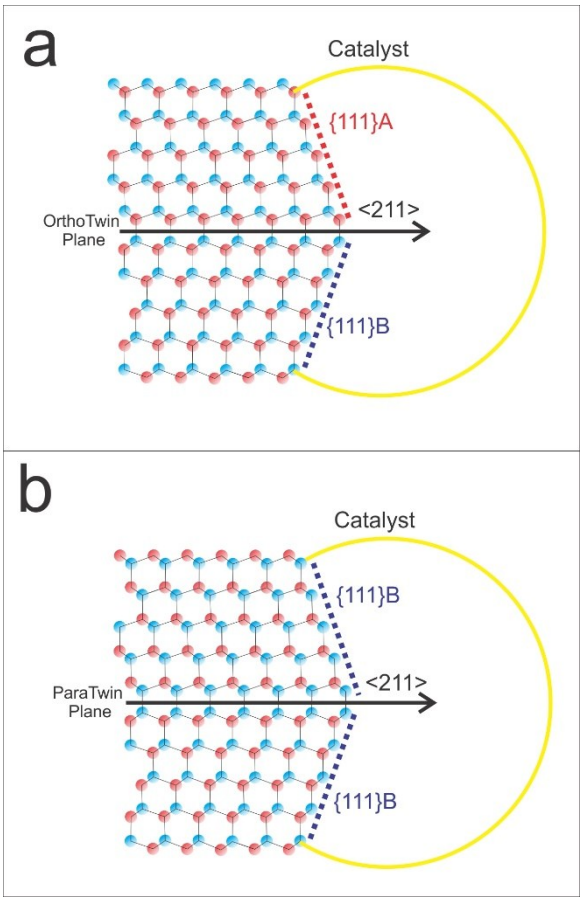

Figure S5. Schematics of the interface between <211>-oriented zincblende InGaP nanowire and the catalyst, from the <110> direction. (a) Nanowire with an ortho-twin. (b) Nanowire with a para-twin.

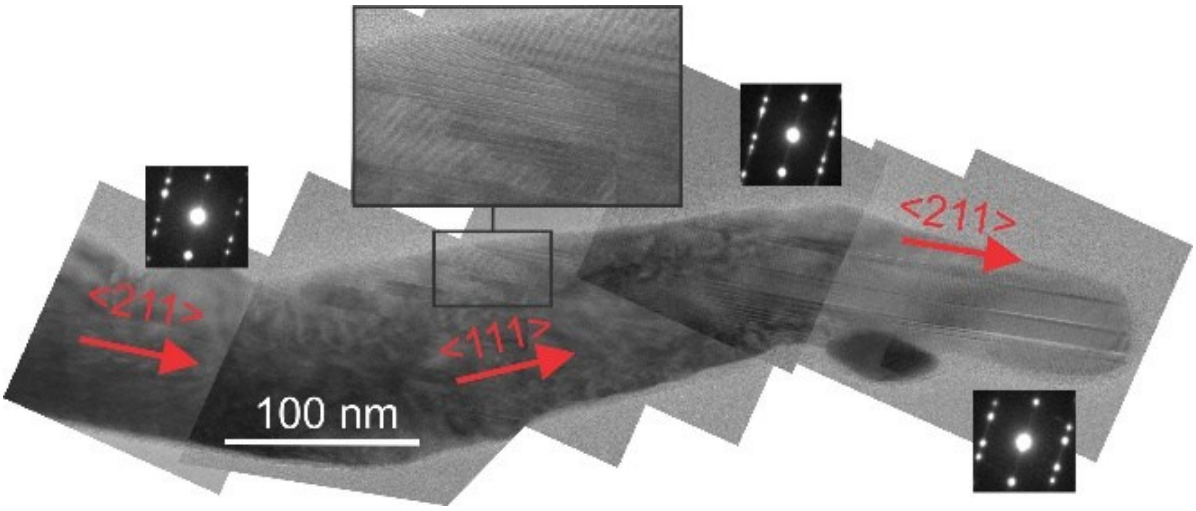

Figure S6. Mosaic of HRTEM images of a nanowire with 2 kinks, from<211> to <111> and from <111> to <211>. The inset shows the starting point of SFs and LT, that are parallel to the last nanowire segment. It may be noticed that even under stationary growth conditions, kinks can be induced by fluctuations of the local growth environment.[1]

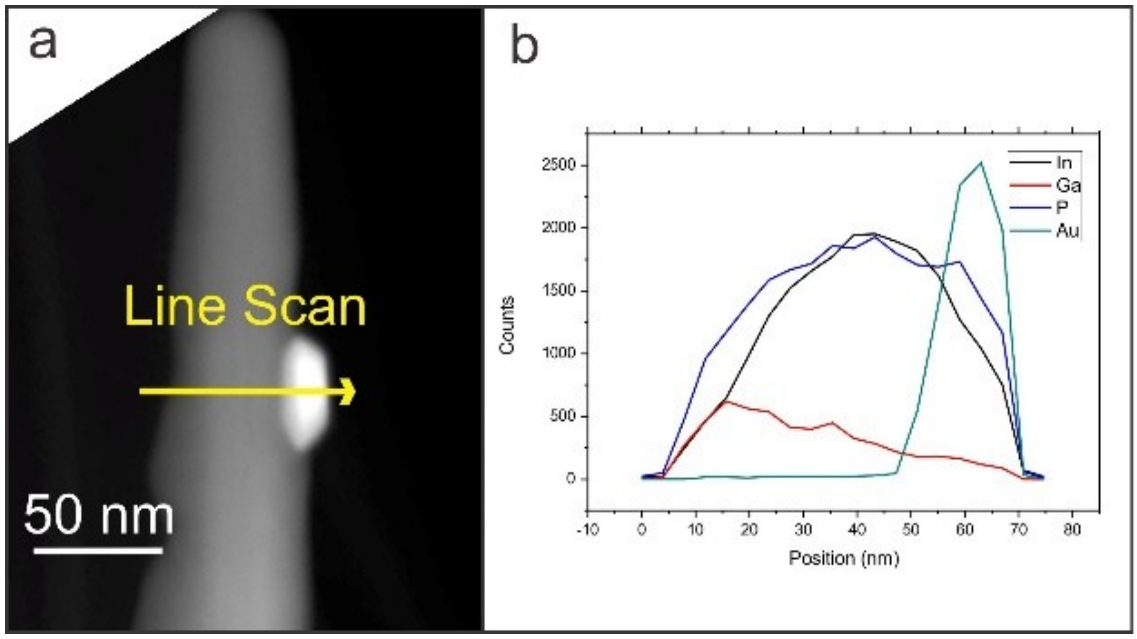

Figure S7.(a) HAADF image of<211>-oriented InGaP nanowire. (b) EDS counts for In, Ga, P and Au along the line scan depicted in (a).

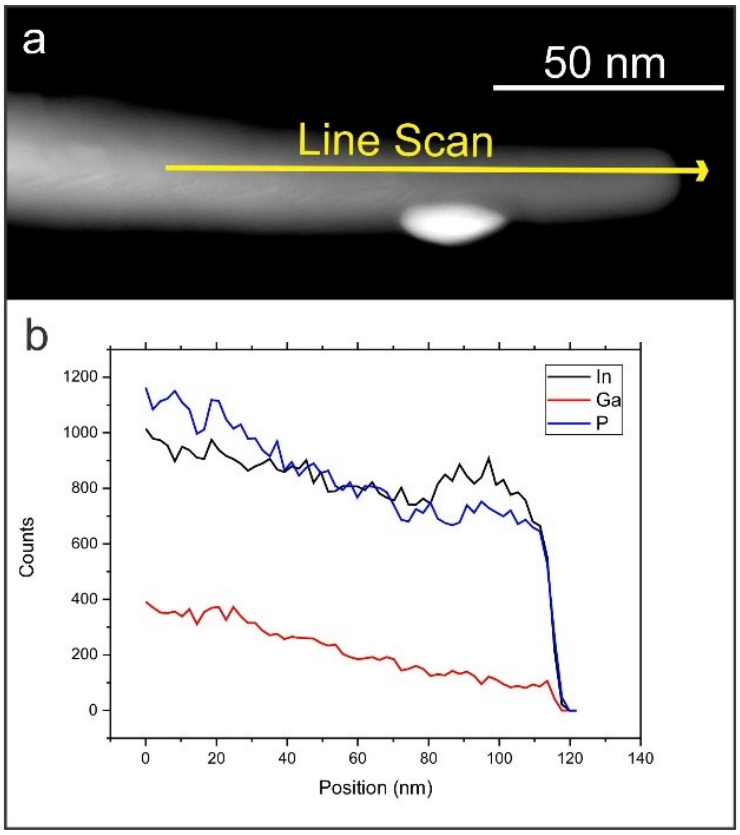

Figure S8. (a) HAADF image of <211>-oriented InGaP nanowire. (b) EDS counts for In, Ga and P along the line scan depicted in (a).

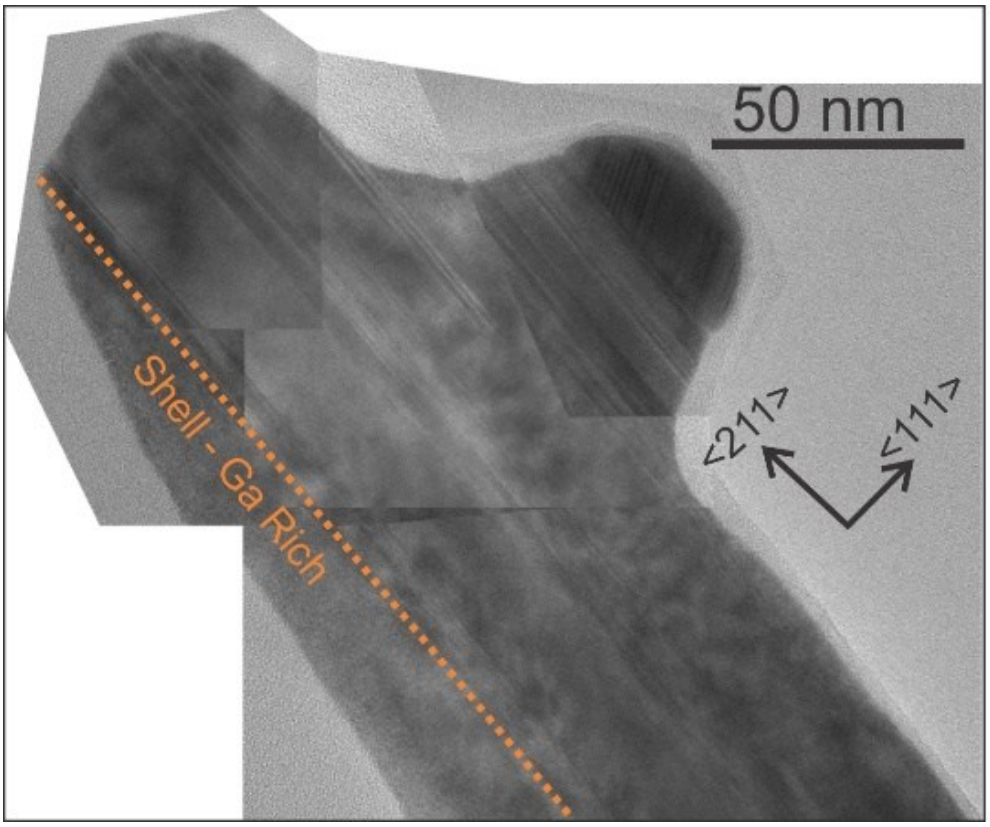

Figure S9. Mosaic of HRTEM images of <211>-oriented InGaP nanowire, with a small branch grown in the <111> direction.

1 K. W. Schwarz and J. Tersoff, *Nano Lett.*, 2011, **11**, 316–20.