## **Supporting Information:**



Figure S1. Diameter distribution of 102 individual NWs observed in the TEM images.

The average NW diameters are determined to be  $34.6 \pm 7.7$  nm from the statistics of 102 individual NWs observed from the TEM images.



Figure S2. (a) HRTEM image of InP NW; same as Figure 2a (scale bar = 5 nm). (b) and (d) FFT images of the separated twin segments as marked in (a). The zone axis of (b) and (d) are indexed as  $[0\overline{11}]$  and [011] respectively. (c) Enlarged HRTEM image of WZ phase segment. The zone axis is marked as  $[2\overline{110}]$ .

Atomic packing of the region marked as (c) in Figure S2 is studied. An ABA arrangement (i.e. WZ structure) rather than ABC arrangement (i.e. ZB structure) of lattice planes is observed along the <111> growth axis. To further confirm this WZ phase segment, the lattice plane distances of **[0002]**, **[0111]** and **[0111]** are measured. The measured distances are 0.34 nm, 0.32 nm and 0.32 nm, respectively (the lattice plane distance of **[0111]** is not marked on Figure S2c). These values match exactly with the calculated values based on the lattice parameters of WZ InP unit cell (a = 4.1423 Å and c = 6.8013 Å) reported by D Kriegner *et al.*<sup>1</sup>

In this regard, the NW shows a mixing of normal ZB, rotated ZB and WZ phases. However, the ratio of WZ phase is relatively low and is not always existed between ZB segments, which explains the reciprocal lattice spots associated with the hexagonal WZ phase are not observed in the FFT shown in Figure 1c (insert).

## **Reference:**

1. D. Kriegner, E.Wintersberger, K. Kawaguchi, J. Wallentin, M. T. Borgstrom, J. Stangl, *Nanotechnology* 2011, **22**, 425704.