

## Electronic Supplementary Information

# Epitaxy-Driven Vertical Growth of Single-Crystalline Cobalt Nanowire Arrays by Chemical Vapor Deposition

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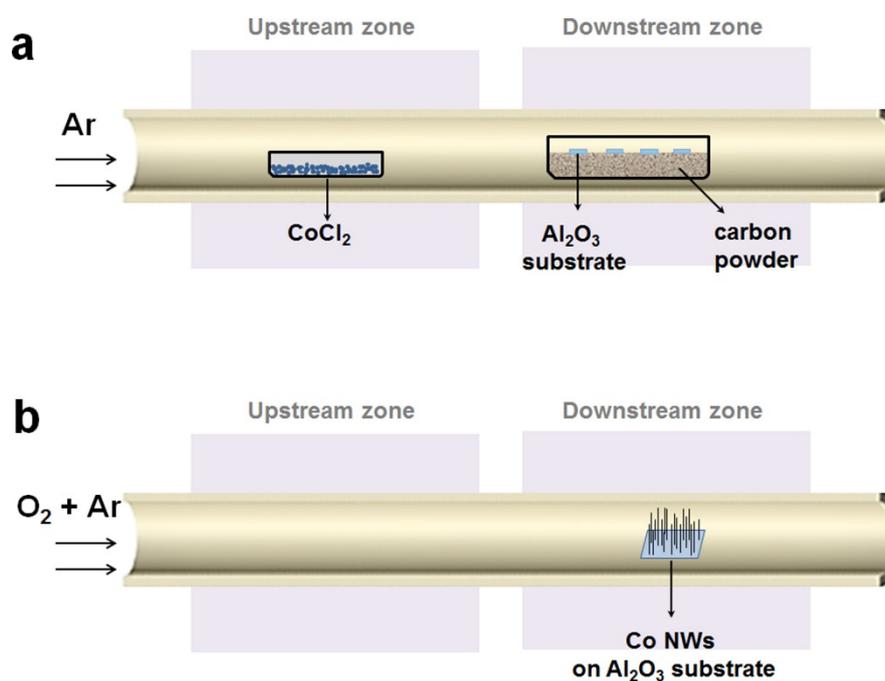
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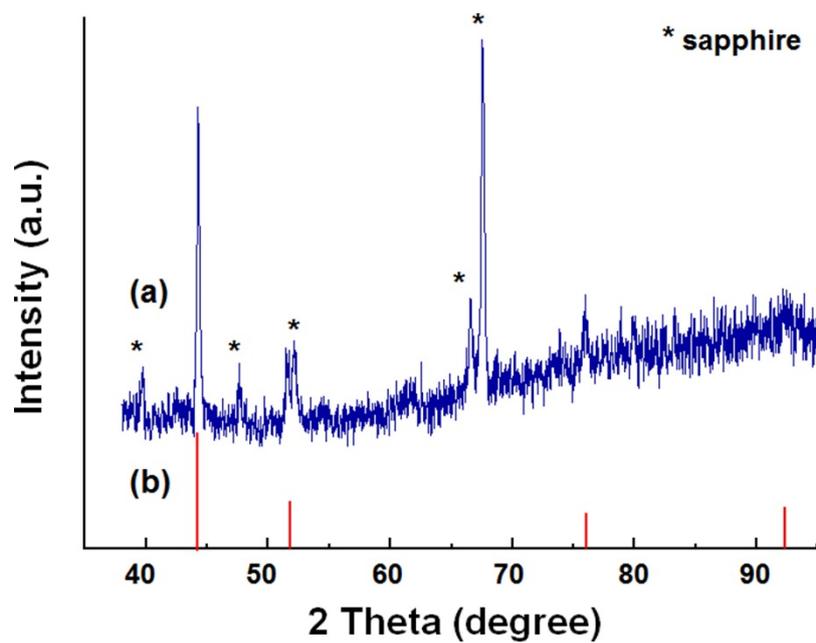
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**Figure S1. Experimental Setup**



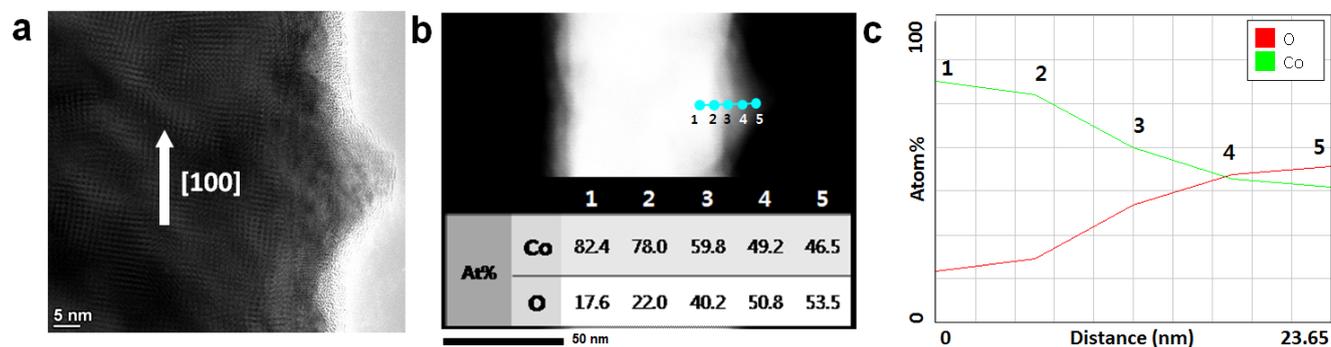
(a) The experimental setup for the synthesis of single-crystalline Co NWs. The setup consists of a horizontal tube furnace with two independently controlled heating zones. (b) The experimental setup for the transformation from Co NWs to  $\text{Co}_3\text{O}_4$  nanotubes in single heating zone.

**Figure S2. XRD pattern of Co NW arrays**



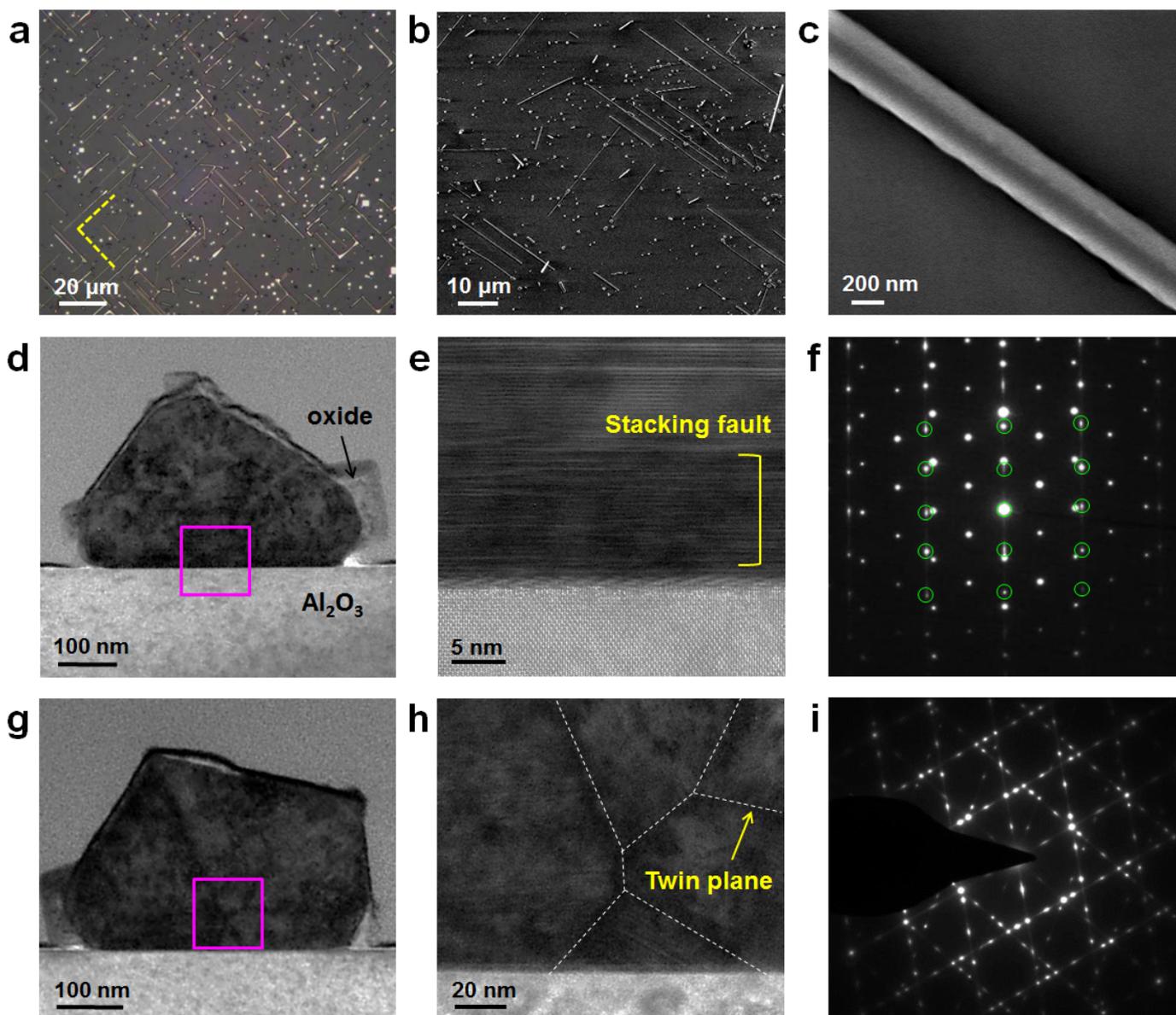
XRD patterns of (a) as-synthesized Co NWs on the *m*-cut sapphire substrate compared with (b) the standard diffraction peaks of face-centered cubic Co. The asterisks represent the diffractions of rhombohedral Al<sub>2</sub>O<sub>3</sub> (sapphire).

**Figure S3. Chemical composition of cobalt oxide in NW surface**



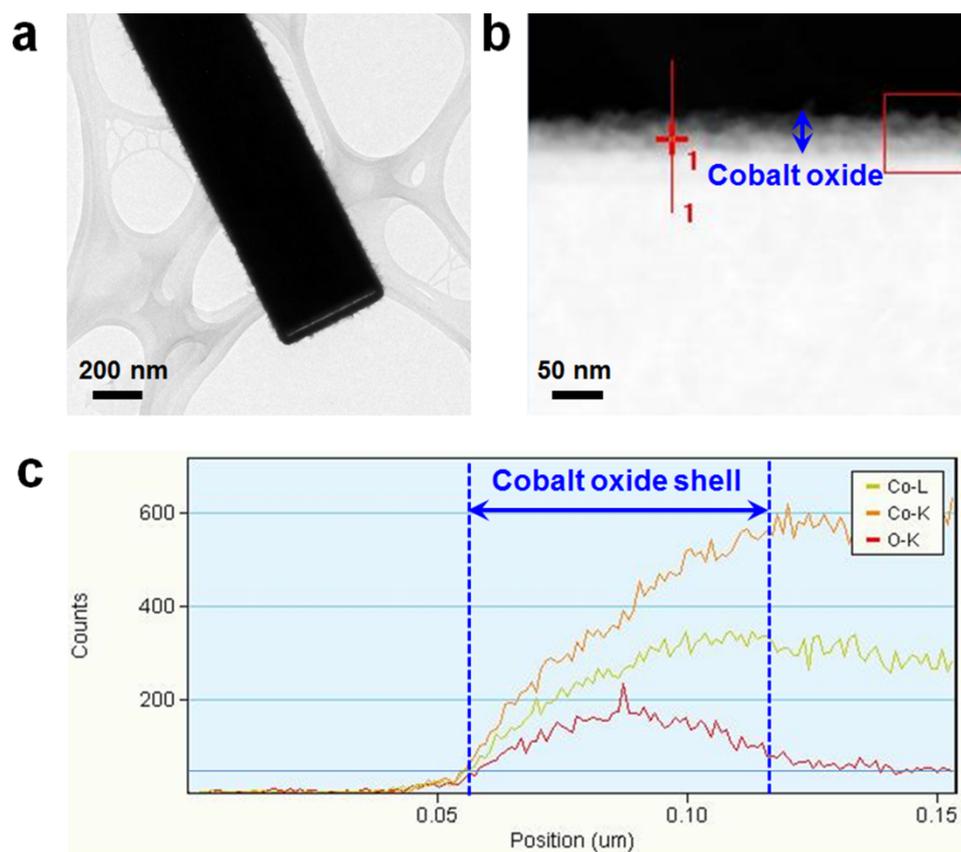
Point EDS analyses for five points over the inner and outer regions of NW. (a) HRTEM image of vertical Co NW along  $\langle 100 \rangle$  direction. (b,c) Atomic ratio of Co and O elements at the five points of 1, 2, 3, 4, and 5 in a Co NW. Since point 1 and 2 include Co core as well as oxide shell, Co was detected in high atomic ratio at this points. On the other hand, the atomic ratio of Co and O is close to 1:1 in point 4 and 5, where oxide shell is only designated, revealing that shell has CoO phase. No peaks were observed in all points except Co and O elements, indicating that intentional catalyst were not employed for synthesis of NW.

**Figure S4. Horizontal Co NWs grown on a *r*-cut sapphire substrate**



(a) Optical microscope and (b) top-view SEM images of horizontal Co NW arrays, which have two orientations at  $90^\circ$  to one another (indicated by yellow dashed line in (a)). (c) Magnified top-view SEM images of horizontal NWs. (d) Cross-section low-resolution TEM image of twin-free Co NW. (e) HRTEM image of pink square in (d). (f) SAED pattern of region including Co NW and sapphire substrate. The green circles represent the diffraction spots reflected from the part of hexagonal close-packed Co NW. Stacking faults, which are a common defect in crystals, are observed from HRTEM image and diffraction pattern analysis. (g) Low-resolution TEM image of twinned Co NW. (h) HRTEM images of pink square in (g). The NW has five-fold twinned structure, indicated by white dashed lines. (i) SAED pattern of twinned region.

**Figure S5. Co@CoO NW obtained by thermal annealing at 400 °C**



(a) Low-resolution TEM image of Co@CoO core-shell NW structure synthesized on the condition of 400 °C for 10 min. (b) STEM image of NW in (a). Contrast difference shows that thickness of cobalt oxide layer is ~50 nm. (c) EDS line profiles of regions including core and shell parts along the red line in (b).