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Atomistic Exploration of the Surface-Sensitive Oriented Attachment Growth of α-MnO_2 Nanowires and the Formation of Defective Interface with 2×3 and 2×4 Tunnel Intergrowth

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Understanding the surface sensitivity during nanostructure growth in solution environment is important for better design of different structures.[1] In particular, how tunnel-based oxide nanoparticles self-assemble along specific surfaces with the tunneled structure well aligned along the formed interface is not fully explored. Oriented lateral attachment by self assembly of α-MnO_2 nanowires is proposed as one of the many competing mechanisms explaining the growth process of one dimensional (1D) α-MnO_2 nanowires in solution.[2] Until now, no uniform conclusion has been made to demonstrate the growth mechanism, which is partly due to insufficient atomistic understanding around the growth-induced defective surface/interface in α-MnO_2.

In this paper, cryptomelane α-MnO_2 nanowires are synthesized via a hydrothermal reaction and characterized using a state-of-the-art aberration corrected scanning transmission electron microscope (Figure 1). Ultramicrotomed cross-sectional slices of α-MnO_2 with length less than 100 nm are obtained to enable atomic scale electron microscopy of α-MnO_2 tunneled structure along the tunnel direction [001], which is also the nanowire's axial direction. α-MnO_2 structure featured by empty 1×1 tunnels and one column K^+-supported 2×2 tunnels is clearly shown at atomic resolution under [001] zone axis view. {100} planes function as the lateral surfaces of single α-MnO_2 nanowire with the lowest surface energy, leading to a square shaped morphology of the nanowire. Oriented attachment mechanism dominates the growth of α-MnO_2 nanowires in solution via lateral attachment of primary α-MnO_2 nanorods sharing their {110} surfaces that are energetically unstable in solution environment. Defective {110} interfaces are thus formed inside secondary α-MnO_2 nanowires and are composed of various 2×3 and 2×4 tunnel intergrowth structures, where more than one K^+ columns are present to support the larger tunnels. The size increase of the interface tunnel is caused by the addition of extra unsaturated [MnO_x] radicals in solution that form bonds with the dangling bonds at the {110} surfaces. As such, lateral oriented attachment mechanism is confirmed for growth of 1D α-MnO_2 nanostructures and the atomic scale mechanism for the tunnel-directed formation of the {110} OA interface is also clearly demonstrated (Figure 2) for the 2×3 tunnel situation.

References:

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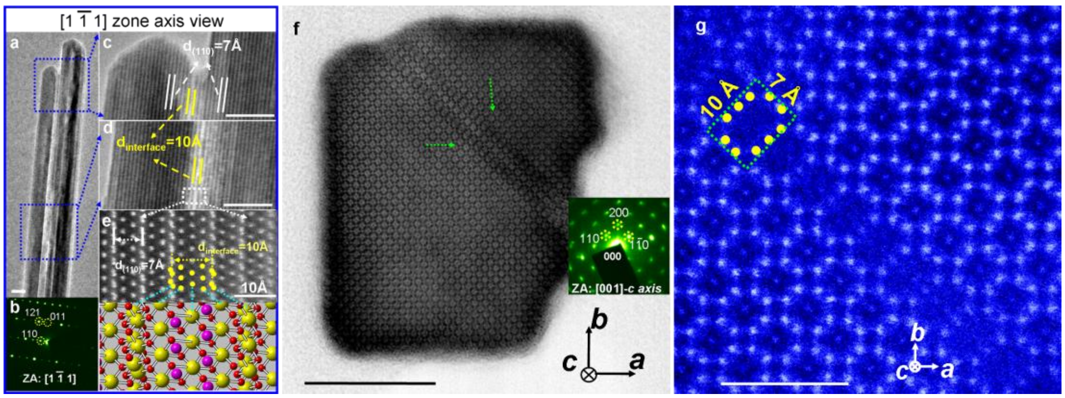

Figure 1. (a-e): Lateral (S)TEM imaging of one secondary α-MnO_2 nanowire after oriented attachment, where (c-e) clearly show the atomic structure along the {110} interface region; the atomic model use yellow spheres for Mn, red for O and pink for K^+. (f, g) Cross-sectional STEM imaging of one sliced nanowire section. The green arrows in (f) indicate the OA interface with its atomic structural shown in (g). Scale bar in(f) is 10 nm, in (g) is 2 nm.[3] "Reprinted with permission from (Y Yuan, S Wood, K He, et al., ACS Nano, 10 (2016), p. 539). Copyright (2016) American Chemical Society."

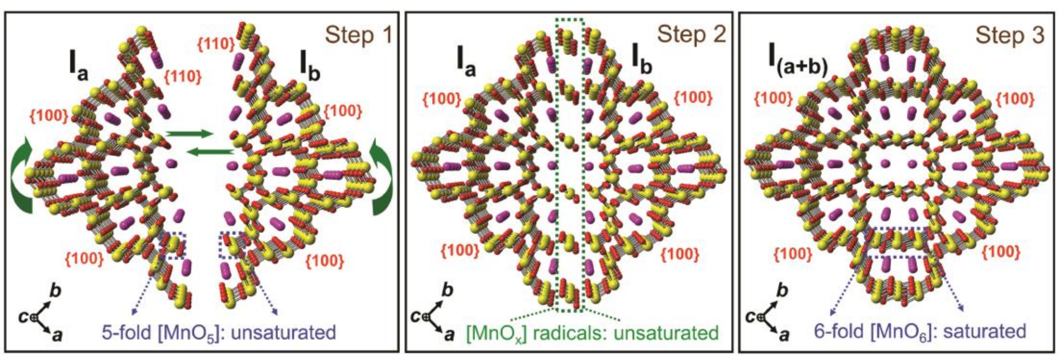

Figure 2. Schematic diagrams illustrating the formation of a 2×3 tunnel-based {110} interface during oriented attachment of two primary α-MnO_2 nanowires (I_a and I_b) at the atomic level. The green arrows in Step One indicate the movement directions of two primary nanowires.[3] "Reprinted with permission from (Y Yuan, S Wood, K He, et al., ACS Nano, 10 (2016), p. 539). Copyright (2016) American Chemical Society."