Synthesis and self-assembly of one-dimensional nanostructures of a transition metal trichalcogenide

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Transition metal trichalcogenides (TMTs) (1) are one-dimensional (1D) layered materials containing trigonal prismatic chains of metals and chalcogens bonded via weak van der Waals (vdW) force (Figure 1a). The materials host several intriguing correlated physics in the bulk, such as charge/spin density waves and superconductivity. However nanostructured forms of TMTs have been rarely explored due to the difficulty in nanomaterial synthesis and assembly (2).

Niobium trisulfide (NbS₃) is one of the least studied members in the family of TMTs, in part because of obstacles in synthesizing the material with a pure phase and controlled composition (3). In a single batch of the crystal growth product, materials with different phases and compositions can coexist, which lead to challenges in studying and understanding both the growth mechanism and the physical properties of the material (4). Moreover, the charge density wave (CDW) transitions and therefore the associated periodic lattice distortions of NbS₃ have been shown to depend on the material's crystal phase (5).

Here we present a bottom-up approach to synthesize nanowires (NWs) of NbS₃, by using an alkaline metal halide salt (6, 7) (sodium chloride, NaCl) as a catalyst. Figure 1 shows the atomic-resolution structure (Figure 1b), electron diffraction (Figure 1c) and chemical composition (Figure 1d) of a representative NW, confirming that the as-synthesized NW is NbS₃ (5). Aberration-corrected STEM observation (Figure 1e-f) indicates that the NW displays two periodic lattice modulations simultaneously, which hints at its modified electronic structure.

We further demonstrate the tuning of morphologies and self-assembly of NbS₃ nanostructures by changing the growth conditions and substrate chemistry (Figure 2). Figure 2a-b are SEM images of salt-catalayzed NbS₃ NWs, one with a flat surface and rectangular cross section (Figure 2a) and another one with a corrugated surface (Figure 2b), grown under different precursor fluxes. In addition, these NbS₃ NWs can self-assemble into particularly long structures. This can take place at the boundary of different substrate materials, as in Figure 2c which shows end-to-end merging and assembly of NbS₃ NWs at the step edge between the SiO₂ substrate and an h-BN flake. The continuous merging preferentially occurs along the zigzag orientation of h-BN flakes. On the other hand, under high flux synthesis condition, NbS₃ NWs also display long structures. These appear to be formed by synergistic growth, in which one NbS₃ segment grows at the end of another, even with a different height, creating stepped structures with lengths up to tens of micrometers (Figure 2c). We anticipate that controlled growth of high aspect ratio structures like these may prove useful in understanding transport and modulation in this material. Our study paves the way to synthesize nanowires of layered materials and their heterostructures. It also creates a window to investigate different growth modes governing the self-assembly of these low-dimensional quantum materials (8).

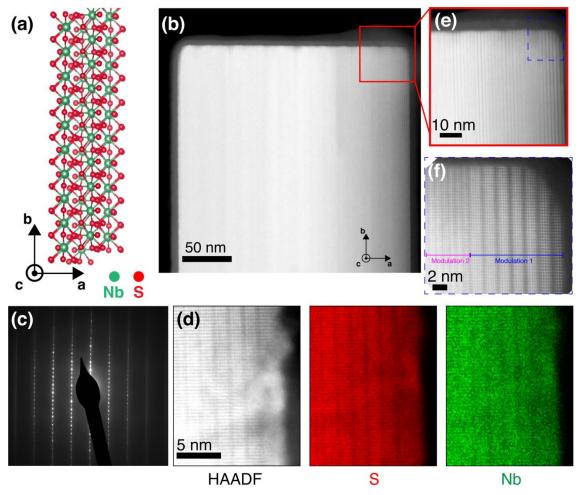


Figure 1. Figure 1. Nanowires of layered materials. (a) Trigonal prismatic structure of NbS3. The material is made of vdW bonded chains of Nb-S. (b) STEM image of a representative NbS3 NW and its electron diffraction (c). (d) STEM-EDS elemental mappings of Nb and S. (e-f) Atomic-resolution STEM images of the NW showing two simultaneous lattice modulations.

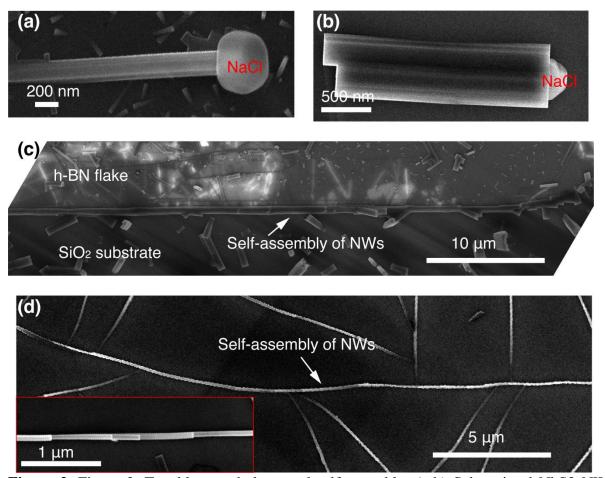


Figure 2. Figure 2. Tunable morphology and self-assembly. (a-b) Salt-assisted NbS3 NWs with two distinct morphologies grown under different fluxes of precursors. (c) Self-assembly of NbS3 NWs at the step edge of two different substrate surface chemistries. (d) Synergistic assembly of NbS3 NWs on SiO2 substrate, creating long and stepped NWs. (Inset) Steps on an assembled NW.

References

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