Mechanism of WS2 nanotube formation revealed by in-situ/ex-situ imaging and cross-sectional sequences

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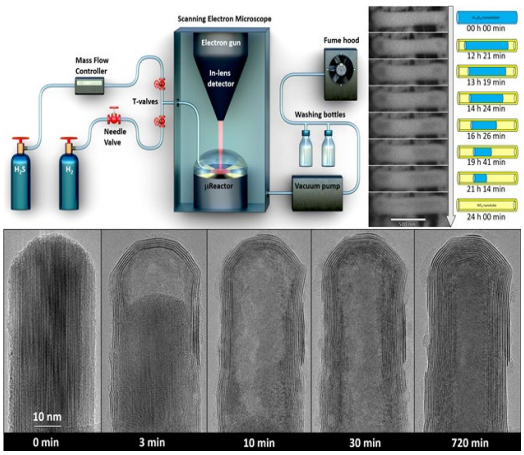
Multiwall WS_2 nanotubes have been synthesized from $W_{18}O_{49}$ nanowhiskers in substantial amounts for over a decade [1]. The established growth model is based on the "surface-inwards" mechanism, whereby the high-temperature reaction with H_2S starts on the nanowhisker surface, and the oxide-to-sulfide conversion progresses inwards until hollow-core multiwall WS_2 nanotubes are obtained [2]. In the present work, an upgraded in-situ SEM µReactor [3] with an H_2S source has been conceived to study the growth mechanism in detail. Ex-situ TEM technique was developed to gain structural insight to the reaction at selected times. Further inspection was done by cross-sectional ex-situ TEM sequences where preselected long $W_{18}O_{49}$ nanowhisker was observed from the (010) direction during the sulfidation reaction as a series of lamellae.

Based on these techniques, a hitherto undescribed growth mechanism, named "receding oxide core", which complements the "surface-inwards" model, is observed and kinetically evaluated. Initially, the nanowhisker is passivated by several WS_2 layers via the surface-inwards reaction. At this point, the diffusion of H_2S through the already existing outer layers becomes exceedingly sluggish, and the surface-inwards reaction is slowed down appreciably. Subsequently, the tungsten suboxide core is anisotropically volatilized within the core close to its tips. The oxide vapors within the core lead to its partial out-diffuse out, partially, forming a cavity that expands with reaction time. Additionally, the oxide vapors react with the internalized H_2S gas, forming fresh WS_2 layers in the cavity of the nascent nanotube. The rate of the receding oxide core mode increases with temperatures above 900 °C. The growth of nanotubes in the atmospheric pressure flow reactor is carried out, as well, showing that the proposed growth model (receding oxide core) is also relevant under regular reaction parameters. The current study comprehensively explains the WS_2 nanotube growth mechanism, combining the known model with contemporary insight.

Graphic:



Keywords:

WS2-nanotube, in-situ, ex-situ, SEM, TEM

Reference:

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