

Introduction: Nanostructured materials have attracted great interest in recent years because of their unusual mechanical, electrical and optical properties and are becoming increasingly important for electrochemical energy storage. For example, Fig. 1 shows carbon nanotubes coated with silicon layer for applications in lithium ion microbattery devices.

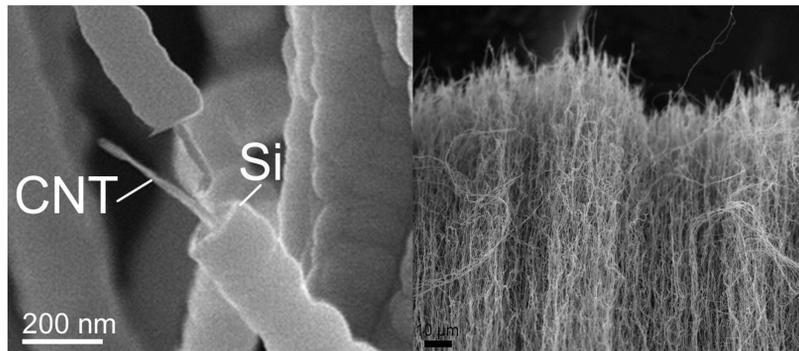


Fig. 1 SEM micrographs of CNT electrode coated with a Si thin film layer. *Yushin et al.*

Project Goal Using vapor-solid-solid (VSS) method to grow nanowires of tungsten oxides without a catalyst for application in lithium-ion microbatteries.

Experimental Tungsten oxide nanowires were synthesized without a catalyst and carrier gas in a hot-walled CVD reactor. Tungsten powder was loaded on a quartz boat and inserted in a tube furnace. The temperature was increased to 950 °C and the pressure was set to 1 mTorr. The growth mechanism is different from the VLS mechanism and template growth mechanism since no external catalysts or solvents were used during the growth process and the nanowires were directly grown on Si/SiO₂ substrates.

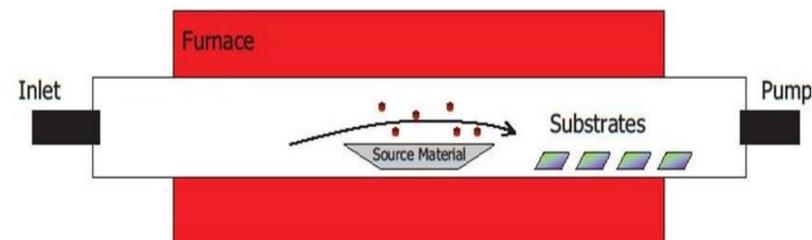


Fig. 2 Schematic of the hot-walled chemical vapor deposition used in the synthesis of the tungsten oxide nanowires.

Other Method of growing nanowires: Vapor-liquid-solid (VLS) is a well known method for the growth of nanowires. However, a catalyst is required which leaves impurities in the nanostructured materials (see fig. 3) which may affect the properties of the battery.

Vapor Liquid Solid (VLS) growth

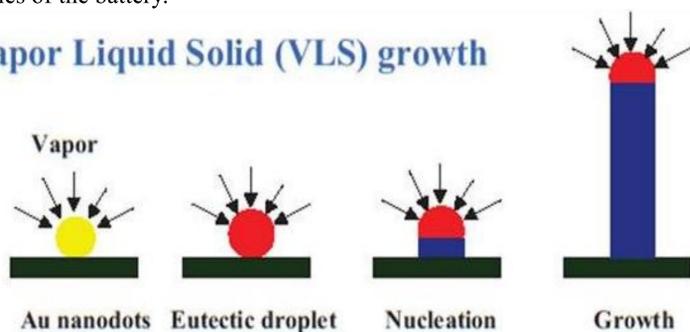


Fig. 3 Illustration of the VLS method showing the catalyst in red and a nanowire in blue.

Results: Based on the XRD and the color of the nanowires (blue), we believe that tungsten is present in mixed-valence state. The XRD spectrum of the sample shows that the reflection peaks belong to the monoclinic crystal structure.

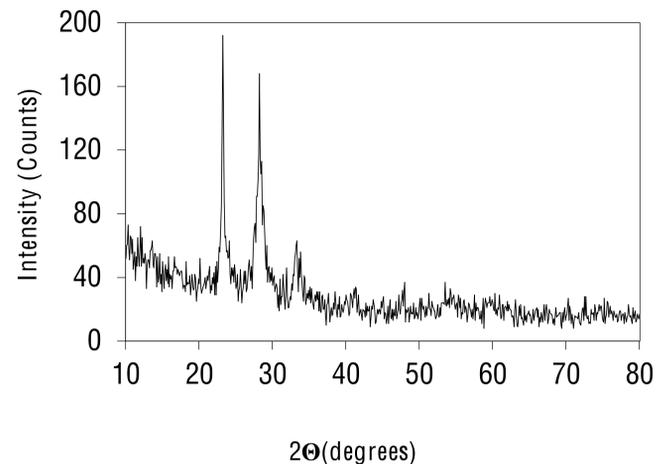


Fig. 4 X-ray diffraction of tungsten oxide nanowires grown on silicon substrates at 644 °C without catalyst or carrier gas.

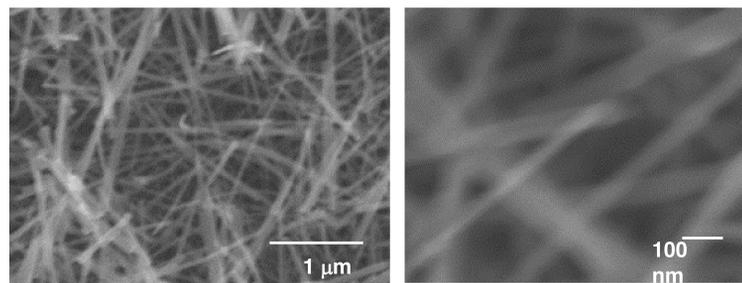


Fig. 5 FE-SEM images of tungsten oxide nanowires deposited without a catalyst or carrier gas.

Fig. 6 below shows similar crystal structure and morphologies when tungsten oxide is evaporated and a carrier gas is used to transport the vapor. In most instances a catalyst is used to obtain the nanowires. (*Wu et al.*)

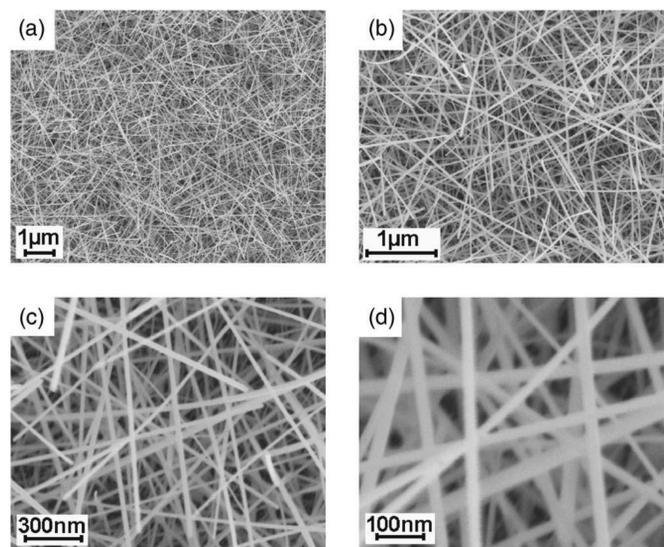


Fig. 6. SEM images below show similar morphologies of WO_{3-x} deposited by thermal evaporation under a carrier gas. (Ref. 1).

When we deposited tungsten oxide under slightly different conditions such as the distance between the substrates and the boat, a mixture of thin film and nanowires is observed. XRD shows that the nanomaterial is amorphous (Fig. 7).

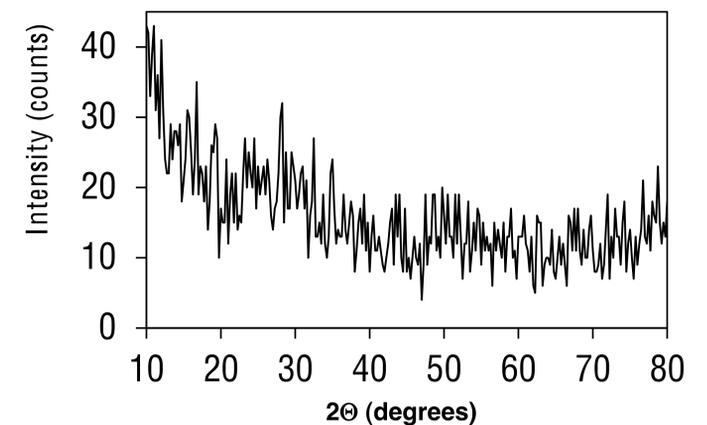


Fig. 7 X-ray diffraction of tungsten oxide nanowires grown on silicon placing at different distances in the tube furnace with temperature at 644 °C without catalyst or carrier gas.

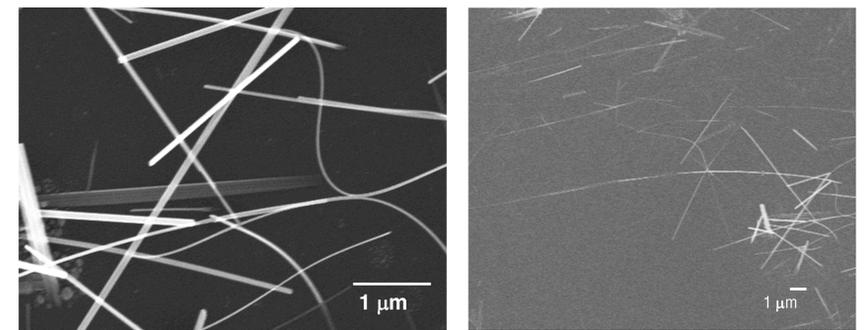


Fig. 8 SEM of WO₃ growing as thin film and nanowires. It is evident that some of the nanowires are very long (>3 micron).

A complete understanding of the VSS growth mechanism is not fully understood. However, we noticed that tungsten oxide vapor flows to the lower temperature zone where the substrate is placed and becomes supersaturated for nucleation of small clusters and for subsequent growth of nanowires. When the pressure of the chamber becomes significantly lower (< 10⁻² torr) so that the mean free path of the tungsten oxide vapor is greatly enhanced, thus supersaturation is increased which enhances nucleation of tungsten oxide nanowires on substrate wafers.

Conclusion Tungsten oxide nanowires were successfully synthesized by thermal evaporation without the presence of a catalyst or carrier gas. The size of the nanowires varied but some nanowires were longer than 4 micrometer. It was found that most of the deposition of the tungsten oxide onto the substrates happens around 12-15 inches from the quartz tube.

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References

1 K. Hong, M. Xie, R. Hu, and H. Wu, *Applied Physic Letters*, 173121, 90 (2007).