# ナノ鋳造法を用いた新奇光応答型スイッチ材料の創出

Nano-Template Growth of Nanowires for Electromechanical Switching Devices

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Since the discovery of buckminsterfullerene in 1985, nanocarbon materials have played a crucial role in modern materials science. Recently, significant efforts have been redirected towards exploring 'post-nanocarbons'. Over the past decade, 2D layers of transition metal chalcogenides have been widely recognized as 'beyond graphene' owing to their versatile chemistry and physics. On the other hand, their 1D counterparts such as ribbons, tubes, and wires could exhibit the unique electrical and optical properties, significantly distinct from 2D transition metal chalcogenides as well as 1D nanocarbons. In particular, isolated wires of transition metal monochalcogenides (TMMs) have been predicted to exhibit variable bandgaps depending on their torsional angles, allowing potential applications such as electromechanical switching devices. However, exploring their potential has been hampered by their limited availability. Although these materials have been prepared using chemical and lithographic methods, the reliable production of well-defined 1D TMMs remains a significant challenge.

Here we report atomically precise fabrication of 1D TMMs within carbon nanotubes (CNTs). Chemical reactions confined inside the nanotubes promote and stabilize the bottom-up growth of 1D TMMs, allowing their easy handling and characterization. We found that choosing suitable precursors and diameters of the host nanotubes provides a feasible yield for their characterization. Atomic-level transmission electron microscopy enabled us to observe dynamic torsions of the TMM nanowires inside CNTs, not seen in the bulk. Furthermore, isolated TMM nanowires exhibit a significant optical absorption in the visible-light region. Our findings suggest that 1D TMMs could provide new building blocks for future nanoelectronics.

## 研究目的

Development of low-power electronic devices will offer opportunities to resolve some issues for energy consumption. Atomically thin wires of transition metal monochalcogenides (TMMs) have been predicted to change their bandgaps from zero to finite values depending on their torsional angles, allowing the innovation of electromechanical switching devices that can consume less power. Despite the growing interest, however, only a tiny amount of the TMM nanowires are currently available, which makes it difficult to explore their potential for switching devices. The purpose of this study is to achieve high-yield syntheses of TMM nanowires and reveal their properties.

## 概　要

Atomically thin 1D transition metal

*mono*chalcogenides (TMMs) have been anticipated as the promising building blocks for channels and switches in integrated nanoelectronics. However, the reliable production of TMM nanowires had eluded scientists over the past few decades. Here we report the bottom-up fabrication of 1D TMMs inside carbon nanotubes (CNTs). We find that the choice of suitable metal oxides as a precursor provides their feasible yields for characterizing their properties. These TMM nanowires exhibit a significant optical absorption in the visible-light region. Moreover, the electronic properties of CNTs can be tuned by encapsulating different TMM nanowires.

Nanocarbon materials, *i.e.*, nanoscale substances comprised of carbon, have played a crucial role in modern materials science. As the nanocarbon research matures, significant efforts have been directed towards creating 'post-nanocarbon' materials. Transition metal chalcogenides have been regarded as the promising candidates for the novel low-dimensional materials owing to their versatile chemistry and physics. Over the last decade, mono- or few layers of transition metal *di*chalcogenides have been widely recognized as the ideal platform to investigate two-dimensional (2D) physics. On the other hand, their 1D counterparts, which exist in a variety of morphologies and compositions, could exhibit the properties that can be differentiated from 1D nanocarbons. For instance, isolated wires of transition metal *mono*chalcogenides (TMMs) – whose generalized formula is MX, in which M is a transition-metal of group 4–10 and X is a chalcogen (S, Se) – are intrinsically metallic, and thus can serve as atomically thin channels for integrated nanoelectronics. Furthermore, their bandgaps have been predicted to change from zero to finite values depending on their torsional angles, allowing potential applications such as novel switching devices. Despite the growing interest, only a tiny amount of isolated TMM nanowires (NWs) are currently available. Early studies reported successful syntheses of MoS- and MoSeNWs by using chemical, epitaxial, and lithographic methods. Very recently, MoTe was also successfully fabricated by vacuum annealing of bulk $MoTe_2$. In most cases, however, the previously reported TMMs existed in a mixture with bulk TMDs, or in bundles, hindering characterization of their individual properties. The reliable production of single-wired TMMs still remains a significant challenge to researchers seeking to illuminate the nature and potential applications of TMMs.

Here we report the template-based growth of two-kinds of TMMs, MoTe- and WTeNWs inside CNTs. Chemically and thermally robust CNTs act as 'nano-test-tubes' for the synthesis of unusual nanomaterials, while the nanotube itself is not involved in the reactions. The 1D confinement at the nanoscale instigates the self-assembly of MoTeNWs similar to other 1D materials such as ladder-like inorganic helixes, ultra-narrow graphene nanoribbons, and atomic $sp^1$-carbon chains (carbynes). Furthermore, the sheaths of CNTs form few covalent bonds with inner products, instead providing a shield against oxidation. Their inert functionality allows easy handling and accurate characterization of the as-produced wires for future technological advancements. Atomic-level resolution

transmission electron microscopy revealed the torsional waves in the isolated wires, not seen in the bulk. This bottom-up synthesis approach offers better control over the nanoscale properties of TMM nanowires compared to previously reported top-down methods.

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