

A metallic phase of elemental chalcogens: One-dimensional crystals of sulfur inside carbon nanotubes

A one-dimensional (1D) crystal, the ultimate monatomic wire, is one of the most intriguing quantum systems in solid-state physics, and offers a rich potential to pave the way for next-generation electronic nanodevices. As clearly found in a hypothetical 1D hydrogen crystal, which is believed to exhibit a metallic character, synthesis of 1D crystals is a potentially promising approach for transformation of non-metals into metals.

A common problem found in free-standing 1D crystals is the metal-insulator transition, the so-called Peierls transition. It is well known that 1D conducting polymers (e.g., polyacetylene) undergo bond length alternation owing to the Peierls instability, so that the resulting material has a fundamental energy gap. Our strategy for suppressing the Peierls transition is to encapsulate 1D crystals inside the cylindrical nanocavity of carbon nanotubes (CNTs) in order to preserve the enclosed 1D crystal as a 1D quantum conductor.

Carbon nanotubes (CNTs) are ideal containers because of their inherent quasi-1D hollow structures with diameter of ~1 nm. The steric confinement effect due to the constraining nanospace of CNTs has enabled exotic atoms to form a unique nanostructure differing from the bulk structure. In addition, CNTs provide uniform interaction potential fields inside the cylindrical cavity since the lattice of CNTs consists of only carbon atoms. This is in stark contrast to other 1D porous materials, and results in stabilization of the enclosed 1D crystals without any local distortions by the host lattice.

Here, we demonstrate the formation of unprecedented 1D crystals of elemental sulfur inside single-walled CNTs (SWCNTs) and double-walled CNTs (DWCNTs) [1]. The most striking achievement in our study is that the 1D sulfur crystals exhibit a metallic character under ambient pressure, whereas the bulk sulfur requires ultrahigh pressures of above 90 GPa to become metallic. An important property of elemental sulfur is its ability to form covalently bonded 3D helical molecules. However, this fibrous allotrope is an insulator under ambient conditions (Fig. 1(a)). Even though the 1D zigzag and linear configurations have been predicted to show metallic behavior (Fig. 1(b)) [2], to the best of our knowledge, the experimental isolation of these 1D systems has eluded scientists.

As clearly visualized in Fig. 2, high-resolution transmission electron microscopy (HRTEM) revealed the formation of monatomic sulfur chains inside the

hollow cores of an SWCNT (S@SWCNT) and DWCNT (S@DWCNT). Figure 2(a) displays an HRTEM image of two monatomic sulfur chains encapsulated inside an SWCNT with a diameter of 1.1 nm. However, because electron-beam irradiation activated the sulfur chains and induced their translational motion during imaging, the precise bonding configuration of the sulfur atoms inside the single carbon wall was obscured at atomic resolution. To identify the structure of sulfur chains, double carbon walls are useful because the surrounding carbon walls allow us to identify the encapsulated structure with atomic resolution not only by stabilizing the encapsulated sulfur chains, but also by protecting them from electron-beam damage. Here, we can identify a zigzag sulfur chain inside a DWCNT with an inner diameter of 0.7 nm (Fig. 2(b)) and a linear sulfur chain in a DWCNT with a narrower inner diameter of 0.6 nm (Fig. 2(c)). Our HRTEM analysis revealed that the periodic distance is 0.33 \pm 0.03 nm for the zigzag sulfur chain and 0.18 ± 0.02 nm for the linear sulfur chain; the narrower the nanotube diameter, the more constrained the sulfur chain is along the tube axis.

One of our important results is the successful observation of X-ray diffraction (XRD) from the encapsulated 1D sulfur chains (Fig. 2(d)), measured at beamline BL02B2. The XRD result clearly indicates the presence of highly crystalline 1D phases of elemental sulfur in bulk quantity. The domain size of the 1D sulfur chains inside SWCNTs is 35-45 nm, and that in DWCNTs is 90-160 nm at 300 K, indicating that the long-range order and large domain size of 1D sulfur chains is likely to be due to the strong covalent bond within the 1D sulfur chains. In this sense, the "1D monatomic chains" of sulfur are no longer simple chains and we believe that the 1D sulfur chains can be regarded as a new phase of "1D crystals." Note that our XRD analysis showed good agreement with the periodic distances evaluated by HRTEM analysis. In addition, we found that the 1D sulfur crystals formed



Fig. 1. Schematic illustrations of (a) 3D helical sulfur chain that behaves as an insulator and (b) 1D linear and zigzag sulfur chains. These 1D planar configurations exhibit metallic properties at ambient pressure [2].



Fig. 2. HRTEM images of (a) S@SWCNT, (b) S@DWCNT with the 1D sulfur chain in the zigzag configuration, and (c) S@DWCNT with the 1D sulfur chain in the linear configuration. Scale bar: 2 nm. (d) XRD patterns of S@SWCNTs, empty SWCNTs, S@DWCNTs, and empty DWCNTs. Arrows indicate the Bragg peaks of 1D sulfur crystals.

inside SWCNTs and DWCNTs are similar to each other, except for slight axial compression inside the DWCNTs (e.g., the lattice constants *d* of the 1D linear sulfur are 0.197 nm and 0.192 nm inside SWCNTs and DWCNTs, respectively).

Most importantly, we verified that the 1D sulfur crystals indeed exhibit a metallic character, thus improving the electrical conductivity of CNT sheets (Fig. 3). Our temperature-dependent electric-resistance measurements clearly show that the presence of the 1D sulfur crystals reduces the electrical resistivity of both SWCNTs and DWCNTs in the whole temperature range measured here. For instance, we observed that the resistivity of SWCNTs decreases by one-half from 1.1×10^{-3} to $5.0 \times 10^{-4} \,\Omega\cdot$ cm at 300 K, and the drop was more pronounced at 2 K $(1.5 \times 10^{-2} \text{ to } 2.0 \times 10^{-3} \,\Omega\cdot$ cm). We further evaluated the dimensionality of percolation paths due to electron hopping and found that the 1D sulfur crystals

contribute to new conduction paths. These results led us to conclude that the 1D sulfur crystals act as a new metallic phase consisting only of elemental sulfur at ambient pressure.

We have also reported that not only sulfur but also selenium has the ability to form a 1D crystal inside the narrow cavity of DWCNTs [3]. Interestingly, this 1D phase of selenium exhibits the double-helix structure, and its electronic structure differs significantly from that of bulk selenium consisting of a 3-fold single helix. We foresee that the present findings will open new avenues leading to the discovery of new 1D systems, which is a promising way to transform non-metals into metals, resulting in a new branch of nanoscience in the area of exotic 1D crystals inside CNTs.



Fig. 3. Temperature-dependent electric resistivity curves of empty SWCNTs, S@ SWCNTs, empty DWCNTs, and S@DWCNTs.

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