Structure of Sulfur Chains Isolated in Single-Walled Carbon Nanotubes

MD Saiful Islam*
Dept. of Physics, University of Toyama, Toyama 930-8555, Japan
**d24c8202@ems.u-toyama.ac.jp*

Sulfur, like other chalcogens, exhibits a hierarchical structure in which covalently bonded primary units assemble into bulk structures through weak inter-unit interactions. Confinement within single-walled carbon nanotubes (SWCNTs) enables the formation of low-dimensional sulfur allotropes that are unstable in free space. Previous studies on encapsulated Se and Te revealed intra-chain bond shortening and strengthening, highlighting the importance of inter-chain interactions. Here, we investigate the structure of sulfur confined in SWCNTs using X-ray absorption fine structure (XAFS) spectroscopy.

S@SWCNTs were synthesized by vacuum-sealing a sulfur–SWCNT mixture in a forked glass tube and annealing at 873 K for 48 h. Sulfur K-edge XAFS measurements were carried out in transmission mode at the beamline BL-9A of the Photon Factory (KEK, Tsukuba, Japan) over 28–300 K. To interpret the experimental spectra, first-principles XANES calculations were carried out for linear, zigzag, and helical sulfur chain models confined in a (7,7) SWCNT using the all-electron WIEN2k code within density functional theory (GGA–PBE). The systems were modeled using a periodic supercell of 16 × 16 × 17 Å³, with core-hole effects explicitly included.

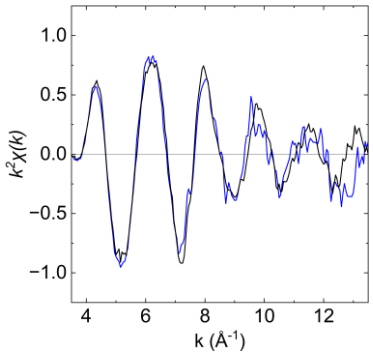

Figure 1: Temperature dependence of the $k^2\chi(k)$ of S@SWCNT at 28 K (black) and 300 K (blue).

Unlike conventional solids, the EXAFS signal of S@SWCNTs exhibits essentially no temperature dependence between 28 and 300 K as shown in Fig. 1. Similarly, neither the bond length nor the MSRD shows any measurable variation with temperature, indicating unusually strong and thermally resilient covalent bonding. The average S–S bond length is 2.057 ± 0.004 Å, indistinguishable from bulk α-sulfur, despite confinement within SWCNTs. This is in contrast with Se- and Te-filled SWCNT systems, which show bond shortening and a temperature-dependent MSRD. The experimental XANES spectrum and theoretical simulations for different sulfur chain models are compared in Fig. 2. A helical configuration is inconsistent with the observed two-peak post-edge structure of the experimental spectra, while both zigzag and linear models reproduce the main spectral features.

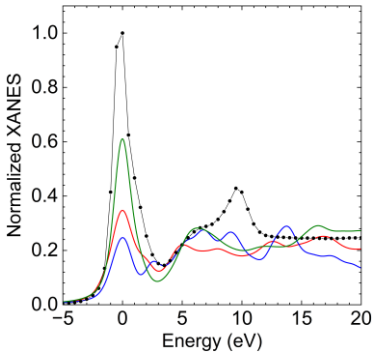

Figure 2: The experimental XANES spectrum of S@SWCNT (black) compared with theoretical spectra for zigzag (red), linear (blue), and three-turn helix (green) sulfur chains confined within SWCNTs.