Encapsulation of Octahedral Molybdenum Clusters and SnSe Nanowires in Single-Walled Carbon Nanotubes

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The structural, vibrational, and electronic properties of octahedral molybdenum clusters and tin selenide (SnSe) nanowires encapsulated in single-walled carbon nanotubes (SWCNTs) have been investigated using a combination of high-resolution transmission electron microscopy (HR-TEM), Raman spectroscopy, and density functional theory (DFT) calculations. Encapsulation of $Mo_6Br_{14}^{2-}$ clusters resulted in the formation of loosely bound moieties within wider SWCNTs, forming semi-ordered cluster arrays. In narrower tubes, confinement-induced polymerization resulted in the formation of one-dimensional (1D) structures. In this case, DFT was used to elucidate the possible structure and to characterize the Raman fingerprints of the polymerized clusters. After SnSe encapsulation, HR-TEM images revealed the presence of two distinct types of 1D SnSe nanowires. One type was composed of square (2 x 2) Sn_4Se_4 units, while the other featured a periodic hexagonal Sn_6Se_6 motif with a Mo_6S_6-like structure. Experimental Raman data support theoretical predictions that the Sn_4Se_4 nanowires exhibit specific modes at 151 and 185 cm^{-1}, while the hexagonal Sn_6Se_6 structure is characterized by a mode appearing at ~235 cm^{-1}. Calculations indicated that the Sn_4Se_4 nanowire has an electronic gap of 1.5 eV and the Sn_6Se_6 nanowire has a semi-metallic character. Raman spectra of both cluster@SWCNT and SnSe@SWCNT hybrid samples showed strong suppression of the radial breathing mode of the nanotubes, indicating an interaction between SWCNTs and the encapsulated compounds. The facilities used in this research were part of the Distributed Research Infrastructure INFRAMAT, supported by the Bulgarian Ministry of Education and Science.

References

1. C.A. Slade, A.M. Sanchez, J. Sloan, Nano Lett. 19 (5) (2019) 2979–2984.
2. E. Faulques, N. Kalashnyk, C.A. Slade, A. M. Sanchez, J. Sloan, V. G. Ivanov, Synthetic Metals 284 (2022) 116968.