

Encapsulated Single-Walled Carbon Nanotubes: Atomic Structure and Electronic Properties

General methodology for the synthesis of one-dimensional crystals inside the inner channels of single-wall carbon nanotubes is reviewed. Size dependent nanocrystal structure relations to SWCNT diameters in the range of 1,2 – 2,5 nm are revealed indicating gradual thinning of nanocrystal with decrease of SWNT diameter to a certain limit (~1,3 nm), then the uncharged crystal cannot be fit to the nanotube. Necessity for in-tube charge compensation introduces serious modifications to 1D crystals structure resulting in certain cases in nanometer-scale dipole chains formation. The relationship between the degree of crystallinity of guest 1D crystals, lengths of interatomic bonds 1D crystals and ionic radius was established. It is shown that the structure and crystallinity of the guest compounds in the internal channels of nanotubes is dictated by inconsistency between the parameters of the unit cell of the crystal and an inner diameter of the tube. Moreover the stoichiometry of nanocrystals established by local microanalysis can deviate from that of bulk materials, which indicates possible chemical bonding of the embedded nanocrystals with the walls of the nanotube. Partial coordination of intercalated compounds by SWNT walls was also established by EXAFS and the high angle angular dark field (HAADF) HRTEM data. These data are supported by appearance of a new localized energy level as revealed by X-ray absorption and emission spectroscopies.

The electronic properties of encapsulated single-walled carbon nanotubes were reviewed for various inorganic compounds including 3- and 4d-metal halides and chalcogenides AX_n (where A - Mn, Fe, Co, Ni, Cu, Zn, Ag, Pb, Sn, Cd; X - Cl, Br, I, S, Se, Te). The choice of those was made to cover a wide range of work functions (3.5 to 6 eV), thus allowing to carry out both donor and acceptor doping of SWNTs. According to the optical absorption, valence band photoemission spectroscopy and work function measurements, a Fermi level (FL) shift is observed for composites as compared with the initial value for pristine tubes illustrating a charge transfer between the nanotube and 1D crystal. It was shown that both the chemical nature and the crystal structure of 1D crystal govern interaction between the embedded compounds and SWNT walls. The decrease in the electron density on the walls of the nanotubes causes a change in the work function, which results in a shift of all components in the x-ray photoelectron spectra. The efficiency of transfer of electrons to the localized state depends on an electron affinity on crystal anion and is strongly correlated with the energy gaps between Van Hove singularities. This effect demonstrates the need for describing the electronic structure of the composites beyond the model of rigid band structure.