Raman Spectroscopy: the Electronic Structure of Nanocomposites AB@SWNT (A=Cd, Zn, Pb, B=S, Se, Te)

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The discovery of single-walled carbon nanotubes (SWNTs) have impulsed a worldwide interest arising from their unusual electronic, chemical, optical and mechanical properties and a great potential for application in nanotechnology. It is generally accepted that all the properties of SWNTs strongly depend on the tube's diameter and atomic structure, and can be successfully influenced by chemical modification of their internal channels. Thus, the filling of SWNT channels with electron-donor or electron-acceptor compounds will bring to an increase or, accordingly, decrease of electron density on nanotube walls and, therefore, allows one to control the electronic properties of the system. Moreover, the intercalation of perfect 1D crystals of functional materials into nanotube channels enables one to take advantage of specific properties of nanocrystalline semiconductor, conductive or magnetic nanostructures.

The present study is focused on the controllable growth of continuous nanocrystals of $A^{II}B^{IV}$ and $A^{IV}B^{VI}$ semiconductors (A=Cd, Zn, Pb, B=S, Se, Te) inside SWNT channels (d=1.0-1.4 nm) and the investigation of their effect on electronic properties of obtained nanostructures. The synthetic strategy involves infill of SWNTs by easy-to-decompose metal iodides followed by treating in chalcogen melt. HRTEM imaging and local EDX analysis proved the successful filling of tube channels by chosen materials and the formation of 1D nanocrystals.

The strong upshifts of RBM and G-peaks (up to 12 cm⁻¹) for nanocomposites AI₂@SWNT and AB@SWNT as compare to empty nanotubes detected by Raman spectroscopy ($\lambda_{laser} = 514$, 633 and 785 nm) were ascribed to the charge transfer from SWNT walls to intercalated semiconductor nanocrystals. This effect depends on the acceptor properties of the ion coordinated to carbon wall: the higher the electron affinity of acceptor the larger is the energy upshift in Raman spectrum. As a result, the change of electronic band structure of filled carbon nanotubes confirmed also by optical spectroscopy measurements was observed.