Direct Determination of Chemically Induced Doping Concentrations in (6,5)- Single-Wall Carbon Nanotubes by EPR

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Control over doping of semiconducting Single-Wall Carbon Nanotubes (SWNTs) by (electro-) chemical methods and intrinsic impurities are considered to be crucial for future applications of SWNTs in carbon-based electronics and photonics. Previous indirect all-optical techniques hypothesize charge carrier localization in semiconducting (6,5)-SWNTs following redox chemical $AuCl_3$ doping, which is indicated by spectral and dynamical changes of the S_1 exciton band [1].

Here, we present direct quantitative investigations of chemical impurities by means of electron paramagnetic resonance (EPR). For the as-produced (6,5)-SWNT samples we detected very low signal intensities stemming from two separate radical-like, isolated spin contributions that we assign to defects or residual impurities and which may be associated with what is sometimes referred to as intrinsic p-doping. Their concentration indicates exceptional nanotube quality with only few paramagnetic species per µm nanotube. Upon addition of the doping agent $(AuCl_3)_2$ we observe a linear increase of the EPR signal intensity which we ascribe to localized p-type impurities on the nanotube. However, at higher doping concentrations, the observed signal saturates, before decreasing again and finally vanishing at the highest $AuCl_3$ concentrations. This seemingly puzzling result can be understood in terms of the formation of EPR silent, diamagnetic bi-radicals which start to appear at moderate doping concentrations. We model this behaviour with a stochastic formation of impurity sites in a 1D lattice, yielding good agreement with experimental data. In conclusion, we can confirm charge carrier confinement at low impurity concentrations in SWNTs with potentially far reaching implications for future device applications.

[1] K. H. Eckstein, H. Hartleb, M. M. Achsnich, F. Schöppler, T. Hertel, ACS Nano 11, 10401 (**2017**).