Killer defects in semiconducting SWNTs

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The doping of semiconductors is key for providing electronic and photonic devices with their desired functionality. This comes with the realization, that the failure to successfully dope certain classes of materials "is an important bottleneck for the technological utilization of these materials" in electronic or photonic devices, as succinctly expressed by Zunger [1]. This concern also pertains to the doping of semiconducting single-wall carbon nanotubes (s-SWNTs) where our ability to provide stable and measured concentrations of surplus carriers remains a major challenge.

Current approaches to doping of s-SWNTs are mostly designed around redox chemistry or covalent modification with electron pulling or pushing side-chain functionalities while the use of substitutional impurities has hardly been explored for the purpose of electronic enhancement. Despite the importance of doping for device technologies, however, it appears that our ability to quantify the concentration of impurity site concentrations or their effectiveness in providing surplus free carriers is still rather limited.

To address these shortcomings we have performed spectroscopic investigations of redox- and electrochemically doped (6,5) s-SWNT samples using fluorescence and absorption spectroscopy [2]. Spectroscopically, there appears to be no noticeable difference between these two approaches. In both cases, exciton bands are found to broaden, become asymmetric and shift to higher energies when the electrochemical potential is shifted toward valence or conduction band edges. These observations are consistent with confinement of excitons by a stochastic distribution of impurities, suggesting that doping is in-homogeneous rather than homogeneous. Moreover, our analysis suggests that the interaction of minority carriers with external counterions can provide deep traps in the band gap which act as 'killer defects', capturing free charge carriers and effectively preventing the desired homogenous doping.

We also discuss how the analysis of exciton absorption bands can be applied to quantify impurity level concentrations. In the context of optical spectroscopy this allows to define and clearly distinguish between intrinsic-, weak-, moderate- and heavy-doping regimes. The onset of degenerate s-SWNT doping is determined to be at about $\pm$ 0.1 e nm^{-1}.

The observed generation of deep charge traps by adsorbed counterions can largely be attributed to weak dielectric screening of Coulomb interactions by SWNTs or their environment, a common characteristic of low-dimensional systems. We take this as evidence for serious fundamental challenges which may have far reaching and possibly broader implications for the successful fabrication of functional semiconductor devices from nanoscale materials.

1. A. Zunger, Appl. Phys. Lett **83**, 57-59 (2003).
2. K. Eckstein, H. Hartleb, M.M. Achsnich, F. Schöppler, T. Hertel, ACS Nano **11**, 10401 (2017).