

Kinetics of diazonium functionalization of carbon nanotubes

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Impurities in semiconductors play a key role for enabling device functionality, for example by acting as donors or acceptors for the generation of free charge carriers or by modifying photophysical properties in beneficial ways. Accordingly, the introduction of defect states in covalently functionalized semiconducting single-wall carbon nanotubes (s-SWNTs) has led to the realization of single photon sources at room-temperature and at telecom wavelengths [1]. The mechanism underlying such functionalization has been proposed to consist of two steps, an initial charge transfer followed by covalent bond formation between nanotube and the diazonium radical [2].

However, this two-step mechanism continues to be debated controversially and additional investigations are needed to clarify its nature. This may help to obtain a greater degree of control over reaction outcomes and kinetics.

To further elucidate the reaction mechanism we have thus measured the kinetics of s-SWNT functionalization on a timescale from seconds to days using absorption and photoluminescence (PL) spectroscopy. The samples investigated are mixtures of aryl-diazonium salt solution and nanotube suspension. The latter consist of chirality-selected organic PFO:BPY polymer- or aqueous SDS surfactant-stabilized s-SWNTs.

In aqueous suspensions we observe that the kinetics are characterized by a quasi instantaneous initial decrease of the first subband (S_1) exciton PL signal, followed by a slower recovery of the exciton PL signal from minutes to hours. In addition, we also observe the slow increase of a familiar, red-shifted defect-induced emission band [3]. In contrast, no such defect induced increase of a defect related PL band is observed for organic solvent based nanotube suspensions.

We will discuss these findings in light of prior studies of s-SWNT functionalization and doping [1-4].

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