Abstract

New photonic carbon nanostructures

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The unique optical properties of chirality-sorted single-walled carbon nanotubes (SWCNTs) make them attractive candidates for modern photonic applications. However, their photoluminescent (PL) emission must first be harnessed through careful chemical modification, *i.e.*, covalent attachment of functional groups to their surface. Sorted SWCNT dispersions are prepared either in water with the aid of surfactants or in organic solvents with the aid of conjugated polymers, depending on the intended application. Water-based systems for SWCNT sorting and functionalization are well described in the literature, in contrast to organic-based systems, although in both cases the reaction mechanisms remain unclear.

In this work, improved conditions of chiral sorting of the commercially available SWCNTs using conjugated polyfluorenes in toluene were described. The improvements not only lead to substantial increase of quality and quantity of the close-to monochiral (6,5) and (7,5) SWCNT dispersions, but also allowed to reduce the consumption of the raw SWCNT material and the polymer, as well as time and energy. This was obtained by repeated extraction of the desired SWCNTs in a closed-loop process, allowing to re-cycle the source of nanotubes, polymer and solvent. Then, the high-quality chirally-uniform dispersions in organic solvents were functionalized using radicals originating from decomposition of benzoyl peroxide (BPO). Proper selection of the reactant concentration, temperature and type of solvent allowed to activate one or radical decay pathways, *i.e.* spontaneous or both induced decomposition. The obtained radicals attack the SWCNTs, grafting them with functional groups via C-O or C-C bonds, both leading to distinct emission features in the PL spectra of the SWCNTs. Further, it was shown, that the symmetrically substituted derivatives of BPO create a toolbox for quick and effective attachment of the functional groups to the surface of SWCNTs, allowing control over the attached groups density and light emission wavelength. Notably, the electron-deficient reactants were found the most effective, which corroborated previous finding and allowed for better understanding of the reaction mechanism. Importantly, the presented method was also successfully used to functionalize larger SWCNTs than the (6,5), even though their reactivity is significantly lower.

Keywords: *single-walled carbon nanotubes, conjugated polymers, aryl peroxides, selective extraction, functionalization, photoluminescence*