Engineering Nanocarbon Interfaces for Electron Transfer
by
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Abstract

Electron transfer events involving single-walled carbon nanotubes (SWCNTs) play an integral role in a variety of applications, ranging from nanotube covalent functionalization to SWCNT-based photovoltaics. In the first part of this thesis, we explore ground-state electron transfer events, during the diazonium derivatization of carbon nanotubes, with the objective of modulating the extent of covalent functionalization. We first explore these events theoretically using a kinetic Monte Carlo simulation, with rate parameters evaluated using Gerischer-Marcus theory, in order to examine the extent to which these reactions can be controlled stoichiometrically. We find that heterogeneities in SWCNT chirality populations result in a large variance in the number of covalent defects, even at low conversions, thereby limiting the ability to control these reactions through stoichiometry.

We then experimentally examine the ability to impart an additional degree of control over these reactions through utilization of the adsorbed surfactant layer. Adsorbed surfactants are shown to influence the diazonium derivatization of carbon nanotubes in several ways, including electrostatic attraction or repulsion, steric exclusion, and direct chemical modification of the diazonium reactant. Such coulombic and surfactant packing effects offer promise toward employing surfactants as an aid in controlling the extent of functionalization of carbon nanotubes with aryl diazonium salts.

We subsequently move on to examine excited-state electron transfer events between SWCNTs and fullerenes. In doing so, we design a series of fullerene amphiphiles that are directly utilized for the colloidal dispersion of SWCNTs, thereby ensuring SWCNT-fullerene electronic interaction. Based on experimental results, we develop Marcus theory-based, structure-reactivity relationships, which describe chirality-dependent electron transfer between SWCNTs and the C_{61}, C_{71}, and C_{85} methanofullerenes.

Finally, we explore the ability to self-assemble fullerene molecules into one-dimensional arrays, which could eventually aid in the development of efficient interfaces for both electron transfer and charge carrier extraction in bulk-heterojunction photovoltaics. In this study, we designed and synthesized two novel, asymmetric methanofullerenes that self-assemble in cyclohexane. We show that, through the utilization of dipeptide interactions, it is possible to drive helical self-assembly of fullerodendrimers into high aspect ratio nanorods, which possess diameters of 3.76 ± 0.52 nm and can be several microns in length.

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