ION-BEAM AND MICROWAVE-STIMULATED FUNCTIONALIZATION AND DERIVATIZATION OF CARBON NANOTUBES

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ABSTRACT

Derivatizing carbon nanotubes (CNTs) with other low-dimensional nanostructures is of widespread interest for creating CNT-based nanocomposites and devices. Conventional routes based on wet-chemical oxidation or hydrophobic adsorption do not allow premeditated control over the location or spatial extent of functionalization. Moreover, aggressive oxidative treatments and agitation in corrosive environments lead to CNT shortening, damage, and incorporation of excess impurity concentrations. Thus, it is imperative to explore and develop alternative functionalization methods to overcome these shortcomings. The work presented in this thesis outlines two such methodologies: one based on focused ion irradiation for site-selective functionalization and the other that employs microwave-stimulation for mild, yet rapid and homogenous CNT functionalization.

The utility of 10 and 30 keV Ga^+ focused ion beams (FIB) to thin, slice, weld, and alter the structure and composition at precise locations along the CNT axis is presented. This strategy of harnessing ion-beam-induced defect generation and doping is attractive for modulating chemical and electrical properties along the CNT length, and fabricate CNT-based heterostructures and networks.

A novel approach that utilizes focused ion irradiation to site-selectively derivatize preselected segments of CNTs with controlled micro-/nano-scale lateral spatial resolution is demonstrated. Irradiation followed by air-exposure results in functionalized CNT segments ranging from the nanoscopic to the macroscopic scale. The functional moieties are utilized to site-selectively anchor Au nanoparticles,

fluorescent nanospheres, an amino acid—lysine, a charge-transfer metalloprotein—azurin, and a photoactive protein—bacteriorhodopsin by means of electrostatic or covalent interactions. This approach is versatile and can be extended to obtaining other molecular moieties and derivatives opening up possibilities for building new types of nano- micro-scale CNT-based hybrid devices.

An eco-friendly microwave approach to rapidly functionalize and derivatize CNTs *without the use* of aggressive oxidants is presented. This novel strategy can be easily adapted to derivatize CNTs with nanoparticles synthesized *in-situ* by metal-ion reduction during functionalization—*all in a single processing step*. The functional groups serve as preferred nucleation points during the polyol reduction of metal ions yielding CNTs that are uniformly and homogenously decorated with nanoparticles, while preserving the structural integrity of the CNTs. As illustrative examples of the simplicity of this approach, nanocrystalline Au and *faceted* nanocrystals of Cu_2O and CdS were synthesized on CNTs using different polyols. The nanocrystal-CNT hybrid structures are obtained within a few seconds to a few minutes, in stark contrast to several hours and multiple steps typically needed for CNT functionalization, particle synthesis and assembly. This strategy provides a facile route to attach a variety of nanostructures onto CNTs for tailoring electrical and optoelectronic properties for developing new types of nanodevices and smart composites.